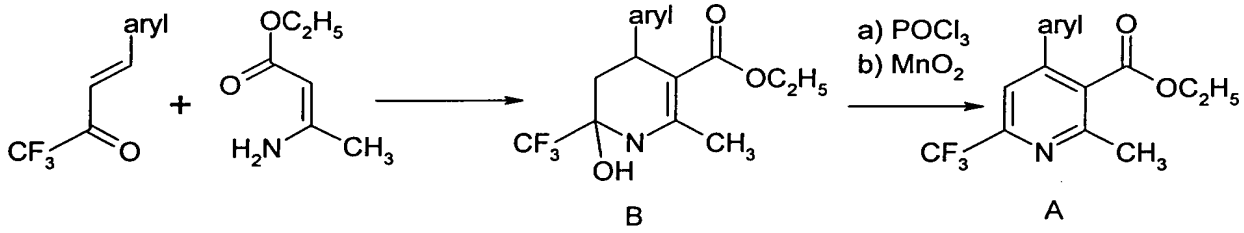
PH/5-70238P1

Process for the preparation of substituted nicotinic acid esters

The present invention relates to a novel process for the preparation of 6-haloalkyl–3-nicotinic acid esters and also to novel enamine intermediates for use in that process.

6-Haloalkyl-3-nicotinic acid esters are valuable intermediates for the preparation of herbicides such as those described, for example, in WO 01/94339.

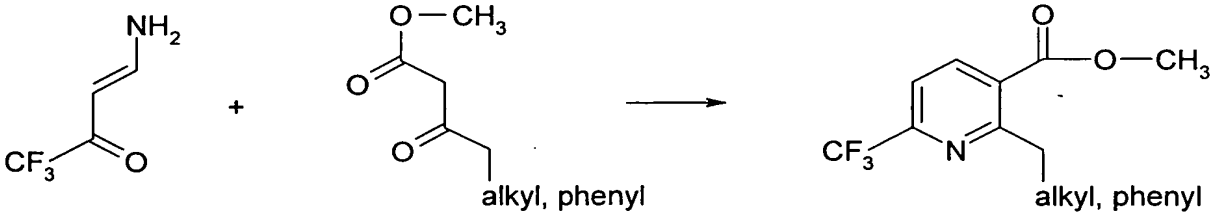
From Heterocycles, Vol. 48, No. 4, 1998, pages 779-785 it is known to prepare 6-trifluoro-3-nicotinic acid ethyl esters substituted by aryl in the 4-position, corresponding to formula A, by means of dehydration and subsequent oxidation of the compound of formula B in accordance with the following scheme



B A

As a result of the uneconomic multi-step procedure, that process is not well suited to the large-scale preparation of 6-haloalkyl-3-nicotinic acid ethyl esters.

According to Heterocycles, Vol. 46, 1997, pages 129-132, 6-trifluoro-3-nicotinic acid methyl esters substituted by phenyl or alkyl in the 2-position, corresponding to formula C,

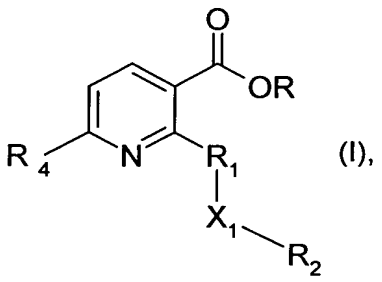


E D C

can be prepared by reacting a compound of formula E with a compound of formula D in benzene and in the presence of trifluoroacetic acid. In addition to unsatisfactory yields, that process has the serious disadvantage for large-scale preparation that the quality of the enamine (E) used as starting material continuously deteriorates during storage as a result of polymerisation reactions, making it considerably more difficult to ensure a consistent product quality.

The problem of the present invention is consequently to make available a novel process for the preparation of 6-haloalkyl-3-nicotinic acid esters which makes it possible to prepare those compounds at reasonable cost, in high yields and with good quality.

The present invention accordingly relates to a process for the preparation of compounds of formula I



(I),

wherein

R is C_1-C_6alkyl;

R_1 is a C_1-C_6alkylene, C_3-C_6alkenylene or C_3-C_6alkynylene chain which may be substituted one or more times by halogen or by R_5, the unsaturated bonds of the chain not being attached directly to the substituent X_1;

R_4 is halomethyl or haloethyl;

X_1 is oxygen, -O(CO)-, -(CO)O-, -O(CO)O-, -N(R_6)-O-, -O-NR_{17}-, thio, sulfinyl, sulfonyl, -SO_2NR_7-, -N$R_{18}$$SO_2$- or -N$R_8$-;

R_2 is hydrogen or C_1-C_8alkyl, or is a C_1-C_8alkyl, C_3-C_6alkenyl or C_3-C_6alkynyl group which may be substituted one or more times by halogen, hydroxy, amino, formyl, nitro, cyano, mercapto, carbamoyl, C_1-C_6alkoxy, C_1-C_6alkoxycarbonyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl, halo-substituted C_3-C_6cycloalkyl, or by C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, C_1-C_6haloalkoxy, C_3-C_6haloalkenyloxy, cyano-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkyl-thio-C_1-C_6alkoxy, C_1-C_6alkylsulfinyl-C_1-C_6alkoxy, C_1-C_6alkylsulfonyl-C_1-C_6alkoxy, C_1-C_6-

alkoxycarbonyl-C_1-C_6alkoxy, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbonyl, C_1-C_6alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylthio, C_1-C_6haloalkylsulfinyl, C_1-C_6haloalkylsulfonyl, oxiranyl (which may in turn be substituted by C_1-C_6alkyl), or by (3-oxetanyl)oxy (which may in turn be substituted by C_1-C_6alkyl), or by benzylthio, benzylsulfinyl, benzylsulfonyl, C_1-C_6alkylamino, di(C_1-C_6alkyl)amino, $R_9S(O)_2O$, $R_{10}N(R_{11})SO_2$-, rhodano, phenyl, phenoxy, phenylthio, phenylsulfinyl or by phenylsulfonyl; it being possible for the phenyl- or benzyl-containing groups to be in turn substituted by one or more C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, halogen, cyano, hydroxy or nitro groups, or

R_2 is phenyl which may be substituted one or more times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, halogen, cyano, hydroxy or by nitro; or

R_2 is C_3-C_6cycloalkyl, C_1-C_6alkoxy- or C_1-C_6alkyl-substituted C_3-C_6cycloalkyl, 3-oxetanyl or C_1-C_6alkyl-substituted 3-oxetanyl; or

R_2 is a five- to ten-membered, monocyclic or fused bicyclic, ring system which may be aromatic, partially saturated or fully saturated and may contain from 1 to 4 hetero atoms selected from nitrogen, oxygen, sulfur, or may contain the group C=O or C=NR_{19}, the ring system being attached to the substituent X_1 directly or by way of a C_1-C_4alkylene, C_2-C_4alkenyl-C_1-C_4alkylene, C_2-C_4alkynyl-C_1-C_4alkylene, -N(R_{12})-C_1-C_4alkylene, -SO-C_1-C_4alkylene or -SO_2-C_1-C_4alkylene group and each ring system containing no more than 2 oxygen atoms and no more than two sulfur atoms, and it being possible for each ring system itself to be substituted one or more times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, mercapto, amino, hydroxy, C_1-C_6alkylthio, C_1-C_6haloalkylthio, C_3-C_6alkenylthio, C_3-C_6haloalkenylthio, C_3-C_6alkynylthio, C_1-C_3alkoxy-C_1-C_3alkylthio, C_1-C_4alkylcarbonyl-C_1-C_3alkylthio, C_1-C_4alkoxycarbonyl-C_1-C_3alkylthio, cyano-C_1-C_3alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylsulfonyl, aminosulfonyl, C_1-C_2alkylaminosulfonyl, N,N-di(C_1-C_2alkyl)aminosulfonyl, di(C_1-C_4alkyl)amino, halogen, cyano, nitro or by phenyl, it being possible for the phenyl group to be in turn substituted by hydroxy, C_1-C_6alkylthio, C_1-C_6haloalkylthio, C_3-C_6alkenylthio, C_3-C_6haloalkenylthio, C_3-C_6alkynylthio, C_1-C_3alkoxy-C_1-C_3alkylthio, C_1-C_4alkylcarbonyl-C_1-C_3alkylthio, C_1-C_4alkoxycarbonyl-C_1-C_3alkylthio, cyano-C_1-C_3alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylsulfonyl, aminosulfonyl, C_1-C_2alkylaminosulfonyl, N,N-di(C_1-C_2alkyl)-

aminosulfonyl, di(C_1-C_4alkyl)amino, halogen, cyano or by nitro, and the substituents on the nitrogen in the heterocyclic ring being other than halogen;

R_5 is hydroxy, C_1-C_6alkoxy, C_3-C_6cycloalkyloxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkoxy or C_1-C_2alkylsulfonyloxy;

R_6, R_7, R_8, R_9, R_{10} R_{11}, R_{12}, R_{17}, R_{18} and R_{18b} are each independently of the others hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbonyl, C_1-C_6-alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkyl substituted by C_1-C_6alkoxy, benzyl, or phenyl, it being possible for phenyl and benzyl to be in turn substituted one or more times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, halogen, cyano, hydroxy or by nitro; R_6 not being hydrogen when R_9 is hydrogen, C_1-C_6alkoxycarbonyl or C_1-C_6alkylcarbonyl;

or the group -R_1-X_1-R_2 together is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6-alkynyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkyl, C_1-C_6haloalkylthio, C_1-C_6haloalkyl-sulfinyl, C_1-C_6haloalkylsulfonyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbonyl, C_1-C_6alkylamino, di(C_1-C_6alkyl)amino, C_1-C_6alkylaminosulfonyl, di(C_1-C_6alkyl)aminosulfonyl, -NH-S-R_{13}, -N-(C_1-C_4alkylthio)-R_{13}, -NH-SO-R_{14}, -N-(C_1-C_4alkylsulfonyl)-R_{14}, -NH-SO_2-R_{15}, -N-(C_1-C_4alkylsulfonyl)-R_{15}, nitro, cyano, halogen, hydroxy, amino, formyl, rhodano-C_1-C_6-alkyl, cyano-C_1-C_6alkyl, oxiranyl, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, C_1-C_6alkoxy-C_1-C_6-alkoxy, cyano-C_1-C_6alkenyloxy, C_1-C_6alkoxycarbonyloxy-C_1-C_6alkoxy, C_3-C_6alkynyloxy, cyano-C_1-C_6alkoxy, C_1-C_6alkoxycarbonyl-C_1-C_6alkoxy, C_1-C_6alkylthio-C_1-C_6alkoxy, alkoxycarbonyl-C_1-C_6alkylthio, alkoxycarbonyl-C_1-C_6alkylsulfinyl, alkoxycarbonyl-C_1-C_6-alkylsulfonyl, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, phenyl, benzyl, phenoxy, phenylthio, phenylsulfinyl, phenylsulfonyl, benzylthio, benzylsulfinyl or benzylsulfonyl, it being possible for the phenyl groups to be substituted one or more times by halogen, methyl, ethyl, trifluoromethyl, methoxy or by nitro;

or the group -R_1-X_1-R_2 together is a five- to ten-membered, monocyclic or fused bicyclic, ring system, which may be aromatic or partially saturated and which may contain from 1 to 4 hetero atoms selected from nitrogen, oxygen and sulfur, the ring system either being attached to the pyridine ring directly or being attached to the pyridine ring by way of a C_1-C_4alkylene chain, and it being possible for each ring system to contain no more than 2 oxygen atoms and no more than two sulfur atoms, and it being possible for the ring system itself to be substituted one, two or three times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_1-C_6alkoxy, C_1-C_6halo-

alkoxy, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, mercapto, C_1-C_6alkylthio, C_1-C_6haloalkylthio, C_3-C_6alkenylthio, C_3-C_6haloalkenylthio, C_3-C_6alkynylthio, C_2-C_5alkoxyalkylthio, C_3-C_5acetylalkylthio, C_3-C_6alkoxycarbonylalkylthio, C_2-C_4cyanoalkylthio, C_1-C_6alkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylsulfonyl, aminosulfonyl, C_1-C_2alkylaminosulfonyl, C_2-C_4dialkylaminosulfonyl, C_1-C_3alkylene-R_{16}, N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, halogen, cyano, nitro, phenyl and by benzylthio, it being possible for phenyl and benzylthio to be in turn substituted on the phenyl ring by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro, and substituents on the nitrogen in the heterocyclic ring being other than halogen;

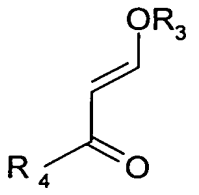
R_{13} is N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_3-C_6cycloalkyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;

R_{14} is N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_3-C_6cycloalkyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;

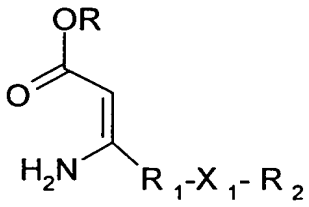
R_{15} is N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_3-C_6cycloalkyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;

R_{16} is C_1-C_3alkoxy, C_2-C_4alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro; and

R_{19} is hydrogen, hydroxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6alkylcarbonyl, C_1-C_6alkoxycarbonyl or C_1-C_6alkylsulfonyl; which process comprises reacting a compound of formula II


(II),

wherein R_3 is C_1-C_8alkyl or C_3-C_6cycloalkyl and R_4 is as defined for formula I, with a compound of formula III


(III),

wherein R, R_1, R_2 and X_1 are as defined for formula I, in an inert solvent in the presence of a proton source.

The alkyl groups appearing in the substituent definitions may be straight-chained or branched and are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl and octyl and also the branched isomers thereof. Alkoxy, alkenyl and alkynyl groups are derived from the mentioned alkyl groups. The alkenyl and alkynyl groups may be mono- or poly-unsaturated.

Halogen is generally fluorine, chlorine, bromine or iodine, preferably fluorine or chlorine. The same is also correspondingly true for halogen in conjunction with other meanings such as haloalkyl or halophenyl.

Haloalkyl groups preferably have a chain length of from 1 to 6 carbon atoms. Haloalkyl is, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, pentafluoroethyl, 1,1-difluoro-2,2,2-trichloroethyl, 2,2,3,3-tetrafluoroethyl or 2,2,2-trichloroethyl; preferably trichloromethyl, difluorochloromethyl, difluoromethyl, trifluoromethyl or dichlorofluoromethyl.

As haloalkenyl there come into consideration alkenyl groups substituted one or more times by halogen, halogen being fluorine, chlorine, bromine or iodine, especially fluorine or chlorine, for example 2,2-difluoro-1-methylvinyl, 3-fluoropropenyl, 3-chloropropenyl, 3-bromopropenyl, 2,3,3-trifluoropropenyl, 2,3,3-trichloropropenyl and 4,4,4-trifluoro-but-2-en-1-yl. Among the C_3-C_{20}alkenyl groups substituted once, twice or three times by halogen, preference is given to those that have a chain length of from 3 to 5 carbon atoms.

As haloalkynyl there come into consideration, for example, alkynyl groups substituted one or more times by halogen, halogen being bromine, iodine or, especially, fluorine or chlorine, for example 3-fluoropropynyl, 3-chloropropynyl, 3-bromopropynyl, 3,3,3-trifluoropropynyl and 4,4,4-trifluoro-but-2-yn-1-yl. Among the alkynyl groups substituted one or more times by halogen, preference is given to those that have a chain length of from 3 to 5 carbon atoms.

Alkoxy groups preferably have a chain length of from 1 to 6 carbon atoms. Alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy or tert-butoxy or the pentyloxy or hexyloxy isomers; preferably methoxy or ethoxy. Alkylcarbonyl preferably is acetyl or propionyl. Alkoxycarbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, isopropoxycarbonyl, n-butoxycarbonyl, isobutoxy-carbonyl, sec-butoxycarbonyl or tert-butoxycarbonyl; preferably methoxycarbonyl or ethoxycarbonyl. Haloalkoxy groups preferably have a chain length of from 1 to 8 carbon atoms. Haloalkoxy is, for example, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy, 2,2-difluoroethoxy or 2,2,2-trichloroethoxy; preferably difluoromethoxy, 2-chlorethoxy or trifluoromethoxy. Alkylthio groups preferably have a chain length of from 1 to 8 carbon atoms. Alkylthio is, for example, methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, sec-butylthio or tert-butylthio, preferably methylthio or ethylthio. Alkylsulfinyl is, for example, methylsulfinyl, ethylsulfinyl, propylsulfinyl, isopropylsulfinyl, n-butylsulfinyl, isobutylsulfinyl, sec-butylsulfinyl or tert-butylsulfinyl; preferably methylsulfinyl or ethyl-sulfinyl.

Alkylsulfonyl is, for example, methylsulfonyl, ethylsulfonyl, propylsulfonyl, isopropyl-sulfonyl, n-butylsulfonyl, isobutylsulfonyl, sec-butylsulfonyl or tert-butylsulfonyl; preferably

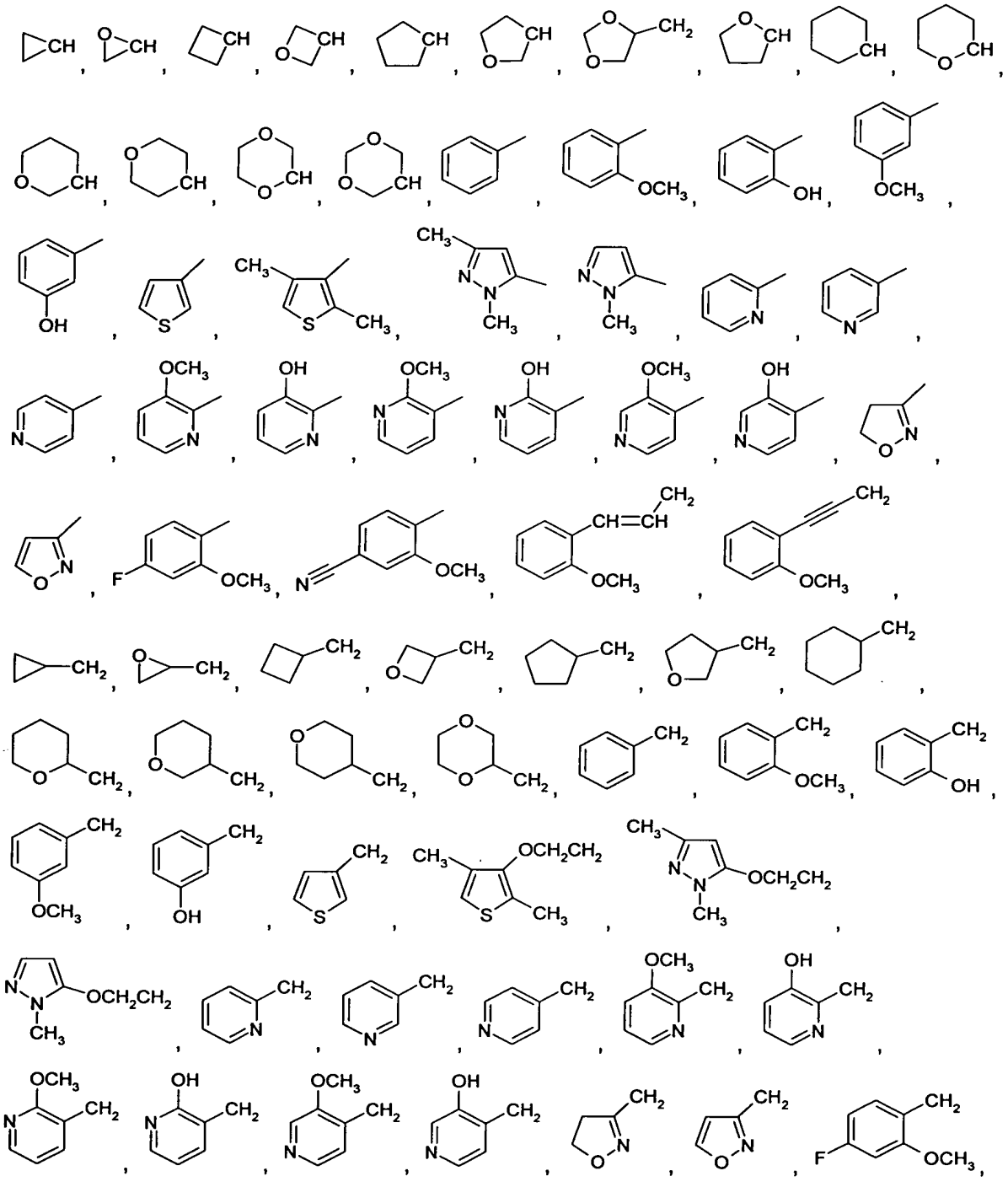
methylsulfonyl or ethylsulfonyl. Alkoxyalkoxy groups preferably have a chain length of from 1 to 8 carbon atoms. Examples of alkoxyalkoxy are: methoxymethoxy, methoxyethoxy, methoxypropoxy, ethoxymethoxy, ethoxyethoxy, propoxymethoxy and butoxybutoxy. Alkylamino is, for example, methylamino, ethylamino, n-propylamino, isopropylamino or the butylamine isomers. Dialkylamino is, for example, dimethylamino, methylethylamino, diethylamino, n-propylmethylamino, dibutylamino or diisopropylamino. Preference is given to alkylamino groups having a chain length of from 1 to 4 carbon atoms. Alkoxyalkyl groups preferably have a chain length of from 1 to 6 carbon atoms. Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl or isopropoxyethyl. Alkylthioalkyl groups preferably have from 1 to 8 carbon atoms. Alkylthioalkyl is, for example, methylthiomethyl, methylthioethyl, ethylthiomethyl, ethylthioethyl, n-propylthiomethyl, n-propylthioethyl, isopropylthiomethyl, isopropylthioethyl, butylthiomethyl, butylthioethyl or butylthiobutyl. The cycloalkyl groups preferably have from 3 to 8 ring carbon atoms, for example cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl. Phenyl, including phenyl as part of a substituent such as phenoxy, benzyl, benzyloxy, benzoyl, phenylthio, phenylalkyl and phenoxyalkyl, may be present in substituted form, in which case the substituents may be in the ortho-, meta- and/or para-position(s). Preferred substituent positions are the positions ortho and para to the ring attachment position.

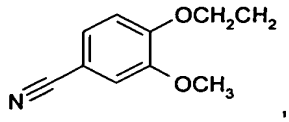
The process according to the invention is especially suitable for the preparation of those compounds of formula I wherein R_1 is $-CH_2-$, $-CH_2CH_2-$, $-CF_2-$, $-CH=CHCH_2-$, $-CH(CH_3)-$ or $-C\equiv CCH_2-$, but preferably $-CH_2-$, the free valency on the left in each case being attached to the pyridine ring.

Preference is furthermore given to the preparation of those compounds of formula I wherein X_1 is oxygen, sulfonyl or a group $-NR_{18}SO_2-$, especially oxygen.

In accordance with the process according to the invention, special preference is given to the preparation of those compounds of formula I wherein R_2 is $-CH_2OCH_3$, $-CH_2OCH_2CH_3$, $-CH_2CH_2OCH_3$, $-CH_2CH_2SO_2CH_3$ or $-CH_2CH_2OCH_2CH_2OCH_3$, preferably $-CH_2CH_2OCH_3$, with very special preference being given to those compounds wherein X_1 is oxygen and R_1 is $-CH_2-$. From that group, those compounds wherein R is ethoxy may be prepared especially advantageously.

Furthermore, in accordance with the process according to the invention there may be advantageously prepared compounds of formula I wherein R_2 is





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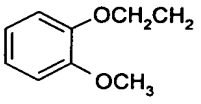

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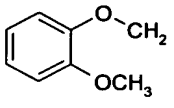


. Where no free valency is indicated in those preferred meanings of R_2, as in the case of, for example,


, the attachment position is at the carbon atom marked "CH".

In the context of the present invention, preference is given to R being methyl, ethyl, n-propyl and isopropyl, especially ethyl.

R_3 is preferably methyl or ethyl, very especially ethyl.

R_4 is preferably trifluoromethyl, difluoromethyl, chlorodifluoromethyl, pentafluoroethyl, 2,2,2-trifluoroethyl, especially trifluoromethyl.

As inert solvents for the method according to the invention there are suitable, for example, aromatic solvents such as benzene, chlorobenzene, fluorobenzene, xylenes, toluene, or alcohols such as methanol or ethanol, and also ethyl acetate, acetonitrile, dimethyl sulfoxide, dimethylformamide, dimethylacetamide, N-methyl-2-pyrrolidone, acetone, butanone, halogenated solvents such as, for example, methylene chloride, trichloromethane, dichloroethylene or trichlorethane, ethers such as tetrahydrofuran, diethyl ether, 1,2-dimethoxyethane, dioxane or methyl tert-butyl ether. Ethanol and toluene are especially preferred.

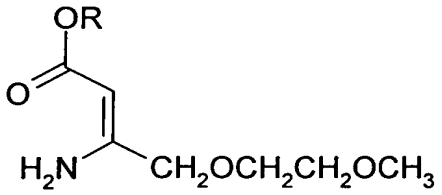
Organic or mineral acids are suitable as the proton source. Examples of suitable proton sources are HCl, HBr, H_2SO_4, carboxylic acids such as acetic acid and derivatives thereof such as trifluoroacetic acid and trichloroacetic acid, sulfonic acids such as methanesulfonic acid or p-toluenesulfonic acid and also carbonic acid. As the proton source for the process according to the invention special preference is given to trifluoroacetic acid.

The reactions can be carried out at ambient temperature or at elevated temperature. In general, addition of the reactants is carried out at a temperature from ambient temperature to the boiling point of the solvent, especially from 20 to 140°C, preferably from 40 to 120°C, with subsequent heating of the reaction mixture, advantageously to the boiling point of the solvent.

The compounds of formula II are known or are accessible by known methods. Processes for the preparation of compounds of formula II are described, for example, in J. Org Chem. (1995) vol 95, 3523, in H. Amil, T. Kobayashi, H. Terasawa, K. Uneyama, Org. Lett. 3(20), 3103-3105 (2001) and also A. Colla, G. Clar, S. Krimmer, P. Fischer, M.A.P. Martins, Synthesis-Stuttgart (6),483-486 (1991).

Some of the compounds of formula III are known. The preparation of such compounds is described in H. G. O. Becker, J. Prakt. Chem. (1961), Vol 12, 294., in WO 00/24714 and also in D.H. Wu, W. Wang, J. Labelled Compd. Rad 39(2),105-107(1997).

The compounds of formula III wherein $-R_1-X_1-R_2$ is $-CH_2-O-CH_2-CH_2-O-CH_3$, that is to say compounds of formula IIIa



(IIIa),

wherein R is as defined for formula III, are novel and were developed specifically for the preparation of compounds of formula I, and the present invention accordingly relates thereto. In a preferred compound of formula IIIa, R is ethyl.

Compounds of formula III can be prepared using processes known to the person skilled in the art, for example by reacting the unsaturated ketones on which they are based with ammonia gas as described in Preparation Example P1 hereinbelow.

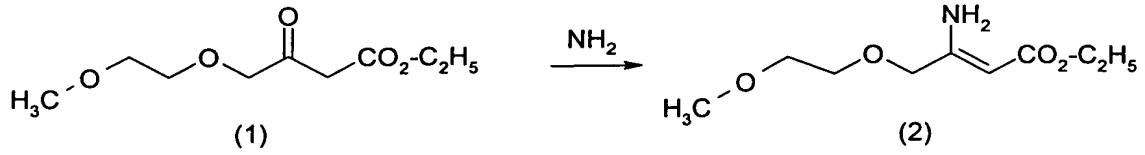
In a preferred embodiment of the process according to the invention, the starting compounds of formula III are prepared from the 3-oxo-carboxylic acid esters on which they are based by introducing ammonia gas and then, without further isolation, reacting directly with the compounds of formula II. That process is especially advantageous for the large-scale preparation of compounds of formula I.

The compounds of formula I either may be used directly in the reaction mixture for further reactions or alternatively may be isolated. Isolation of the compounds of formula I can be

carried out, for example, by extraction of the reaction mixture and subsequent removal of the solvent from the product-containing phase by customary methods.

The process according to the invention will be explained in greater detail in the following Preparation Examples:

Example P1: Preparation of 3-amino-4-methoxyethoxy-but-2-enoic acid ethyl ester:



(1) (2)

A mixture of 1.37 g (6 mmol) of 3-oxo-4-methoxyethoxy-butanoic acid ethyl ester (1) in 13 ml of ethanol is introduced into a reaction vessel and cooled to a temperature of 0°C using an ice/water bath.

Ammonia gas is then introduced for a period of 30 minutes, with stirring, and the reaction mixture is stirred for a further 20 minutes at a temperature of 0°C. After removing the cooling bath, the reaction mixture is allowed to warm up to a temperature of 20°C and ammonia gas is then introduced for a further hour. The reaction mixture is then stirred for 20 hours.

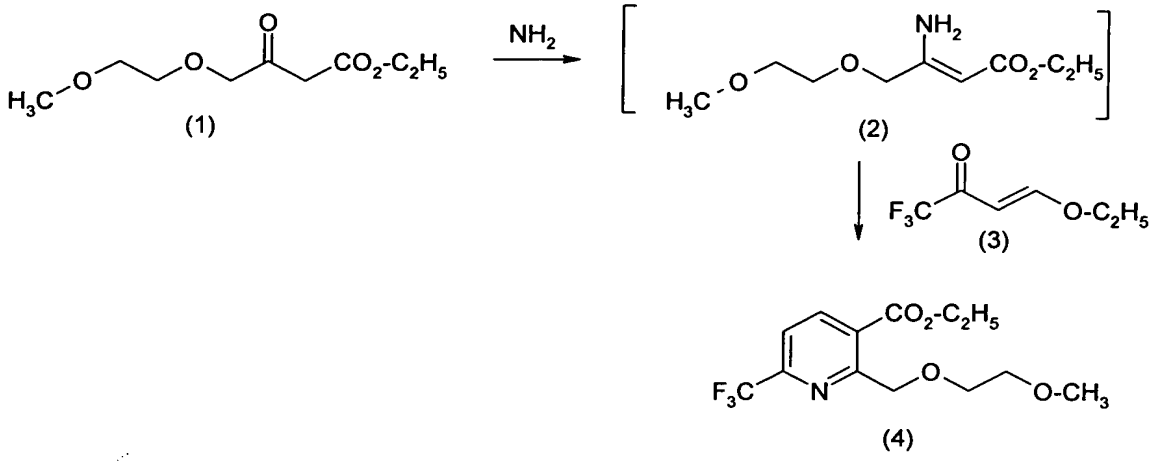
After removal of the solvent *in vacuo*, there are obtained 1.3 g (95 % of theory) of 3-amino-4-methoxyethoxy-but-2-enoic acid ethyl ester (2) in the form of an orange-coloured oil.

^{1}H nmr ($CDCl_3$): 1.30 (t, 3H, $C\underline{H}_3CH_2O$-), 3.40 (s, 3H, $C\underline{H}_3O$-), 3.55 (m, 2H, $OC\underline{H}_2CH_2O$), 3.60 (m, 2H, $OCH_2C\underline{H}_2O$), 4.10 (s, 2H, $C{=}CC\underline{H}_2O$-), 4.15 (q, 2H, $CH_3C\underline{H}_2O$-), 4.50 (s, 1H, $C\underline{H}{=}CNH_2$).

^{13}C nmr ($CDCl_3$): 14.7 (CH_3), 58.9 (CH_2), 59.2 (CH_3), 70.0 (CH_2), 71.0 (CH_2), 71.8 (CH_2), 81.9 (CH), 159.7 (C), 170.3 (C) .

MS: 203 (M^+), 158, 157, 144, 129, 114, 100, 98, 83, 71, 59, 45.

Example P2: Preparation of 2-methoxyethoxymethyl-3-ethyloxycarbonyl-6-trifluoromethyl-pyridine (4):



A mixture of 52.3 g (0.24 mol) of 3-oxo-4-methoxyethoxy-butanoic acid ethyl ester (1) in 150 ml of toluene is introduced into a reaction vessel equipped with a water separator.

Ammonia gas is then introduced into the reaction mixture for 2 hours, with stirring. Refluxing is then carried out for 30 minutes and the water is collected in the separator. After cooling the reaction mixture to a temperature of 20°C, the procedure is repeated. Ammonia gas is again introduced for 1.5 hours, with stirring, and the reaction mixture is then refluxed in order to separate off the water.

After cooling the reaction mixture, which contains 3-amino-4-methoxyethoxy-but-2-enoic acid ethyl ester (2), to a temperature of 20°C, 48 g (0.248 mol) of 1-ethoxy-3-oxo-4-trifluorobutene (3) are added and stirring is carried out at a temperature of 20°C for 18 hours. 1.5 ml of trifluoroacetic acid are then added, stirring is carried out at a temperature of 20°C for 2 hours and refluxing is carried out for a further 2 hours.

The reaction mixture is then allowed to cool down to a temperature of 20°C and is then washed with 100 ml of 1M $NaHCO_3$. The aqueous phase is separated off and is then extracted with 150 ml of toluene and the combined organic phases are then dried over $MgSO_4$.

After removal of the solvent *in vacuo*, there are obtained 65.4 g (62 % of theory) of 2-methoxyethoxymethyl-3-ethyloxycarbonyl-6-trifluoromethylpyridine in the form of a dark-brown oil.

^{1}H nmr ($CDCl_3$): 1.40 (t, 3H, $C\underline{H}_3CH_2O$-), 3.35 (s, 3H, $C\underline{H}_3O$-), 3.55 (m, 2H, $OC\underline{H}_2CH_2O$), 3.70 (m, 2H, $OCH_2C\underline{H}_2O$), 4.45 (q, 2H, $CH_3C\underline{H}_2O$-), 5.00 (s, 2H, $ArC\underline{H}_2O$-), 7.70 (s, 1H, Ar$\underline{H}$), 8.30 (s, 1H, Ar$\underline{H}$).

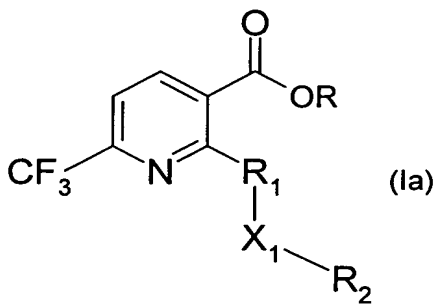
MS: 307 (M^+), 262, 248, 233, 204, 202, 161, 128, 109, 59, 45

The other compounds listed in Table 1 can also be prepared in that manner.

In the following Table, the valency on the left of the radical R_1 is attached to the pyridine ring. When no free valency is indicated in the case of the substituent R_2, as in the case of, for example, 

, the attachment position is at the carbon atom marked "CH".

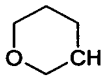
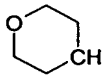
Table 1: Compounds of formula Ia

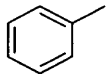
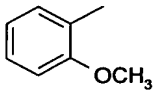
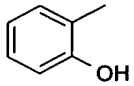
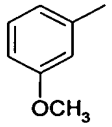
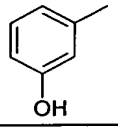
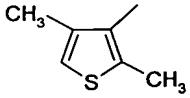
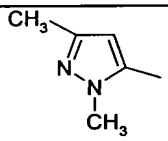
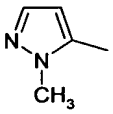
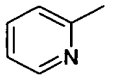
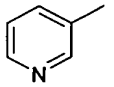
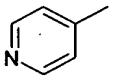
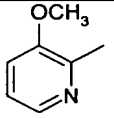
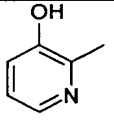


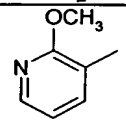
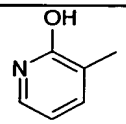
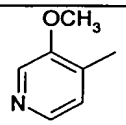
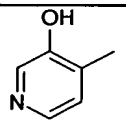
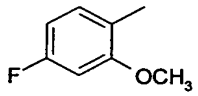
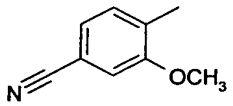
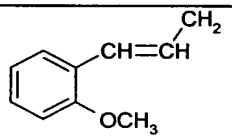
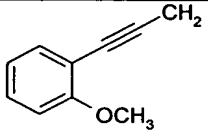
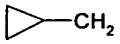
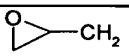
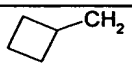
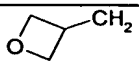
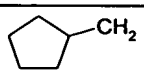
(Ia)

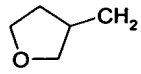
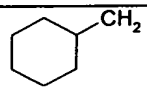
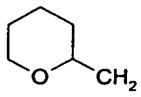
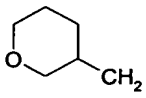
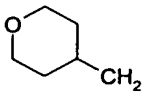
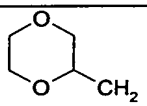
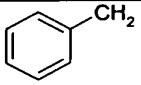
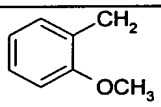
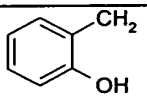
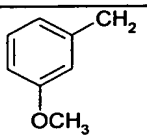
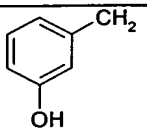
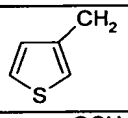
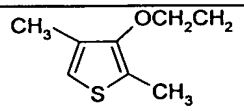
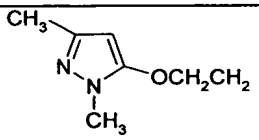
wherein R is ethyl:

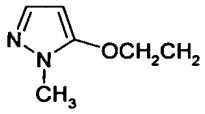
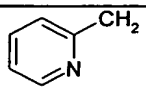
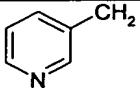
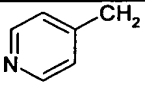
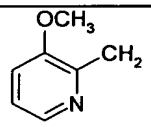
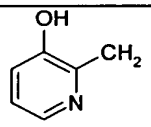
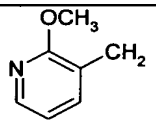
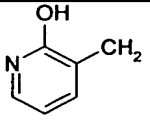
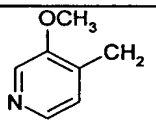
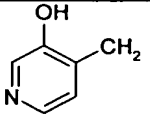
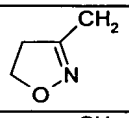
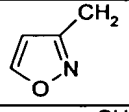
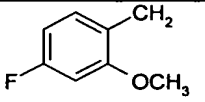
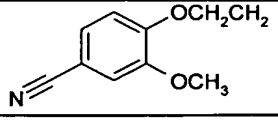
Comp. no.	R_1	R_2	X_1
A1	CH_2	CH_3	O
A2	CH_2	CH_2CH_3	O
A3	CH_2	$(CH_3)_2CH$	O
A4	CH_2	$PhCH_2$	O
A5	CH_2	CH_3	S
A6	CH_2	CH_3	SO

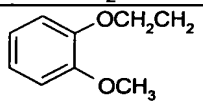
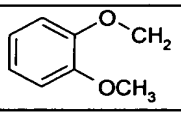
Comp. no.	R_1	R_2	X_1
A7	CH_2	CH_3	SO_2
A8	CH_2	CH_3OCH_2	O
A9	CH_2	$CH_3CH_2OCH_2$	O
A10	CH_2	$CH_3OCH_2CH_2$	O
A11	CH_2	$CH_3CH_2OCH_2CH_2$	O
A12	CH_2	$CH_3OC(CH_3)_2CH_2$	O
A13	CH_2	$CH_3OCH(CH_3)CH_2$	O
A14	CH_2	$CH_3OCH_2CH(CH_3)$	O
A15	CH_2	$CH_3OCH_2C(CH_3)_2$	O
A16	CH_2	$CH_3OCH(CH_3)$	O
A17	CH_2	$CH_3OC(CH_3)_2$	O
A18	CH_2	$HC\equiv CCH_2$	O
A19	CH_2	$H_2C=CHCH_2$	O
A20	CH_2	$CH_3C\equiv CCH_2$	O
A21	CH_2		O
A22	CH_2		O
A23	CH_2		O
A24	CH_2		O
A25	CH_2		O
A26	CH_2		O
A27	CH_2		O
A28	CH_2		O
A29	CH_2		O
A30	CH_2		O
A31	CH_2		O

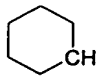
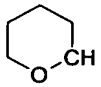
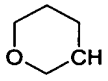
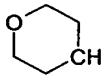
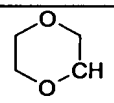
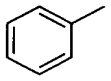
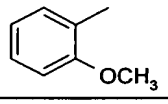
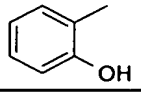
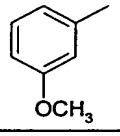
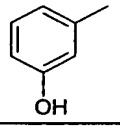
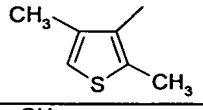
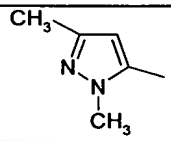
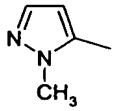
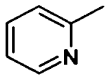
Comp. no.	R_1	R_2	X_1
A32	CH_2		O
A33	CH_2		O
A34	CH_2		O
A35	CH_2		O
A36	CH_2		O
A37	CH_2		O
A38	CH_2		O
A39	CH_2		O
A40	CH_2		O
A41	CH_2		O
A42	CH_2		O
A43	CH_2		O
A44	CH_2		O
A45	CH_2		O

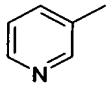
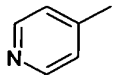
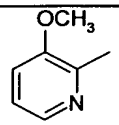
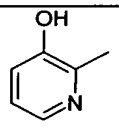
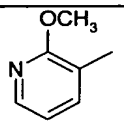
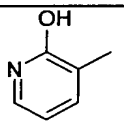
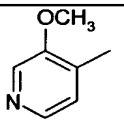
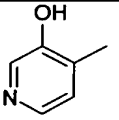
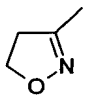
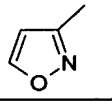
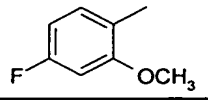
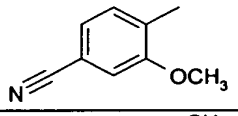
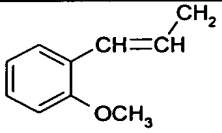
Comp. no.	R_1	R_2	X_1
A46	CH_2		O
A47	CH_2		O
A48	CH_2		O
A49	CH_2		O
A50	CH_2		O
A51	CH_2		O
A52	CH_2		O
A53	CH_2		O
A54	CH_2		O
A55	CH_2		O
A56	CH_2		O
A57	CH_2		O
A58	CH_2		O
A59	CH_2		O
A60	CH_2		O

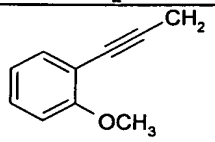
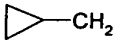
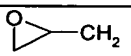
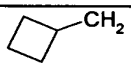
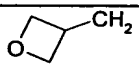
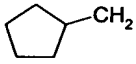
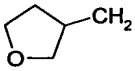
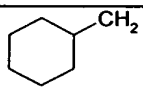
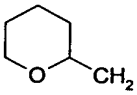
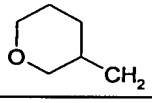
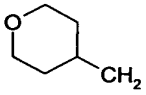
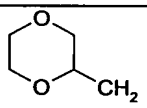
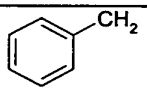
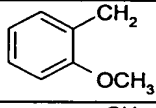
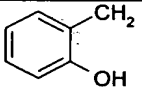
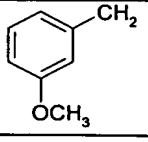
Comp. no.	R_1	R_2	X_1
A61	CH_2		O
A62	CH_2		O
A63	CH_2		O
A64	CH_2		O
A65	CH_2		O
A66	CH_2		O
A67	CH_2		O
A68	CH_2		O
A69	CH_2		O
A70	CH_2		O
A71	CH_2		O
A72	CH_2		O
A73	CH_2		O
A74	CH_2		O

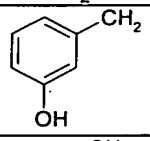
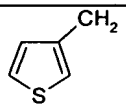
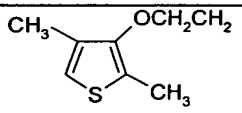
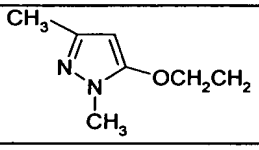
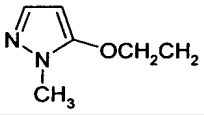
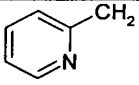
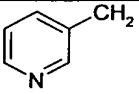
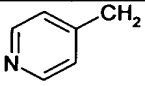
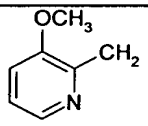
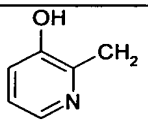
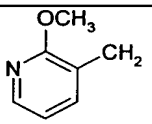
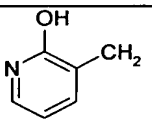
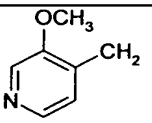
Comp. no.	R_1	R_2	X_1
A75	CH_2		O
A76	CH_2		O
A77	CH_2		O
A78	CH_2		O
A79	CH_2		O
A80	CH_2		O
A81	CH_2		O
A82	CH_2		O
A83	CH_2		O
A84	CH_2		O
A85	CH_2		O
A86	CH_2		O
A87	CH_2		O
A88	CH_2		O

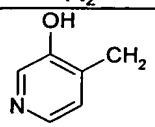
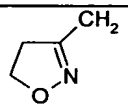
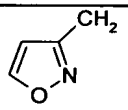
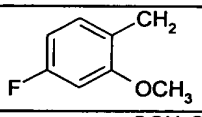
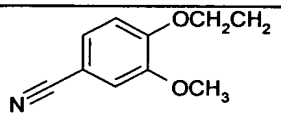
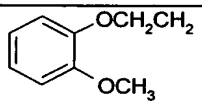
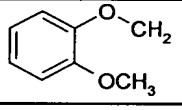
Comp. no.	R_1	R_2	X_1
A89	CH_2		O
A90	CH_2		O
A91	CH_2CH_2	CH_3	O
A92	CH_2CH_2	CH_3CH_2	O
A93	CH_2CH_2	$(CH_3)_2CH$	O
A94	CH_2CH_2	$PhCH_2$	O
A95	CH_2CH_2	CH_3	S
A96	CH_2CH_2	CH_3	SO
A97	CH_2CH_2	CH_3	SO_2
A98	CH_2CH_2	$(CH_3)_2CHCH_2$	O
A99	CH_2CH_2	CH_3OCH_2	O
A100	CH_2CH_2	$CH_3CH_2OCH_2$	O
A101	CH_2CH_2	$CH_3OCH_2CH_2$	O
A102	CH_2CH_2	$CH_3CH_2OCH_2CH_2$	O
A103	CH_2CH_2	$CH_3OC(CH_3)_2CH_2$	O
A104	CH_2CH_2	$CH_3OCH(CH_3)CH_2$	O
A105	CH_2CH_2	$CH_3OCH_2CH(CH_3)$	O
A106	CH_2CH_2	$CH_3OCH_2C(CH_3)_2$	O
A107	CH_2CH_2	$CH_3OCH(CH_3)$	O
A108	CH_2CH_2	$CH_3OC(CH_3)_2$	O
A109	CH_2CH_2	$HC\equiv CCH_2$	O
A110	CH_2CH_2	$H_2C=CHCH_2$	O
A111	CH_2CH_2	$CH_3C\equiv CCH_2$	O
A112	CH_2CH_2		O
A113	CH_2CH_2		O
A114	CH_2CH_2		O
A115	CH_2CH_2		O
A116	CH_2CH_2		O
A117	CH_2CH_2		O

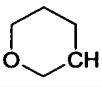
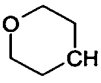
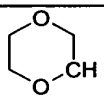
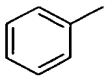
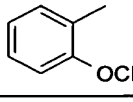
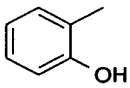
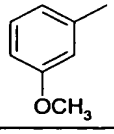
Comp. no.	R_1	R_2	X_1
A118	CH_2CH_2		O
A119	CH_2CH_2		O
A120	CH_2CH_2		O
A121	CH_2CH_2		O
A122	CH_2CH_2		O
A123	CH_2CH_2		O
A124	CH_2CH_2		O
A125	CH_2CH_2		O
A126	CH_2CH_2		O
A127	CH_2CH_2		O
A128	CH_2CH_2		O
A129	CH_2CH_2		O
A130	CH_2CH_2		O
A131	CH_2CH_2		O
A132	CH_2CH_2		O

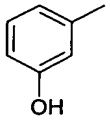
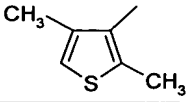
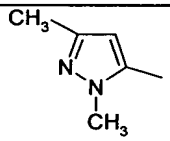
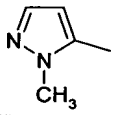
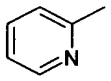
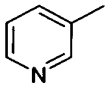
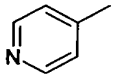
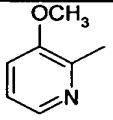
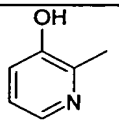
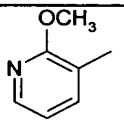
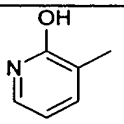
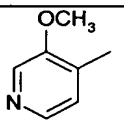
Comp. no.	R_1	R_2	X_1
A133	CH_2CH_2		O
A134	CH_2CH_2		O
A135	CH_2CH_2		O
A136	CH_2CH_2		O
A137	CH_2CH_2		O
A138	CH_2CH_2		O
A139	CH_2CH_2		O
A140	CH_2CH_2		O
A141	CH_2CH_2		O
A142	CH_2CH_2		O
A143	CH_2CH_2		O
A144	CH_2CH_2		O
A145	CH_2CH_2		O

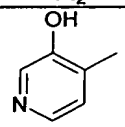
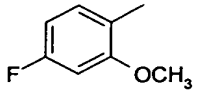
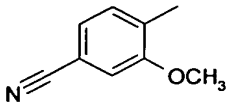
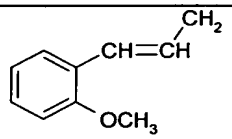
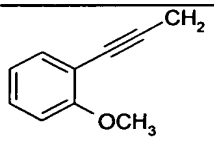
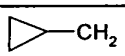
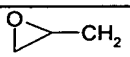
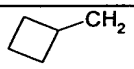
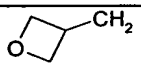
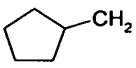
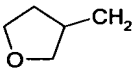
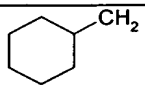
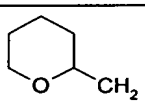
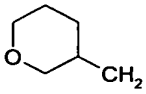
Comp. no.	R_1	R_2	X_1
A146	CH_2CH_2		O
A147	CH_2CH_2		O
A148	CH_2CH_2		O
A149	CH_2CH_2		O
A150	CH_2CH_2		O
A151	CH_2CH_2		O
A152	CH_2CH_2		O
A153	CH_2CH_2		O
A154	CH_2CH_2		O
A155	CH_2CH_2		O
A156	CH_2CH_2		O
A157	CH_2CH_2		O
A158	CH_2CH_2		O
A159	CH_2CH_2		O
A160	CH_2CH_2		O
A161	CH_2CH_2		O

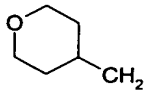
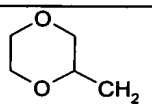
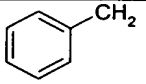
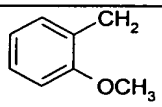
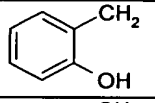
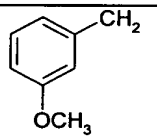
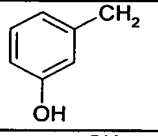
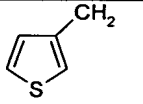
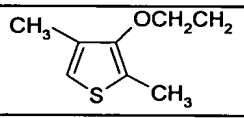
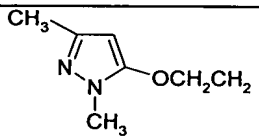
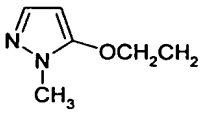
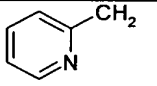
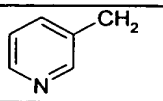
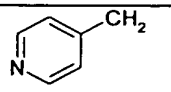
Comp. no.	R_1	R_2	X_1
A162	CH_2CH_2		O
A163	CH_2CH_2		O
A164	CH_2CH_2		O
A165	CH_2CH_2		O
A166	CH_2CH_2		O
A167	CH_2CH_2		O
A168	CH_2CH_2		O
A169	CH_2CH_2		O
A170	CH_2CH_2		O
A171	CH_2CH_2		O
A172	CH_2CH_2		O
A173	CH_2CH_2		O
A174	CH_2CH_2		O

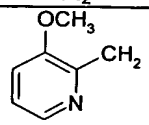
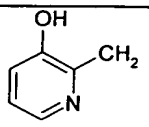
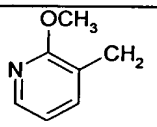
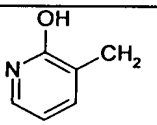
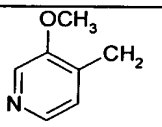
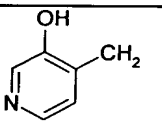
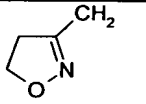
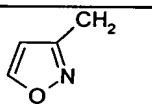
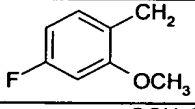
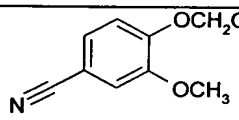
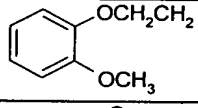
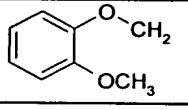
Comp. no.	R_1	R_2	X_1
A175	CH_2CH_2		O
A176	CH_2CH_2		O
A177	CH_2CH_2		O
A178	CH_2CH_2		O
A179	CH_2CH_2		O
A180	CH_2CH_2		O
A181	CH_2CH_2		O
A182	$CH(OCH_3)CH_2$	CH_3	O
A183	$CH(OCH_3)CH_2$	CH_3CH_2	O
A184	$CH(OCH_3)CH_2$	$(CH_3)_2CH$	O
A185	$CH(OCH_3)CH_2$	$PhCH_2$	O
A186	$CH(OCH_3)CH_2$	CH_3	S
A187	$CH(OCH_3)CH_2$	CH_3	SO
A188	$CH(OCH_3)CH_2$	CH_3	SO_2
A189	$CH(OCH_3)CH_2$	$CH_3CH_2CH_2$	O
A190	$CH(OCH_3)CH_2$	CH_3OCH_2	O
A191	$CH(OCH_3)CH_2$	$CH_3CH_2OCH_2$	O
A192	$CH(OCH_3)CH_2$	$CH_3OCH_2CH_2$	O
A193	$CH(OCH_3)CH_2$	$CH_3CH_2OCH_2CH_2$	O
A194	$CH(OCH_3)CH_2$	$CH_3OC(CH_3)_2CH_2$	O
A195	$CH(OCH_3)CH_2$	$CH_3OCH(CH_3)CH_2$	O
A196	$CH(OCH_3)CH_2$	$CH_3OCH_2CH(CH_3)$	O
A197	$CH(OCH_3)CH_2$	$CH_3OCH_2C(CH_3)_2$	O
A198	$CH(OCH_3)CH_2$	$CH_3OCH(CH_3)$	O

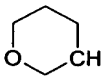
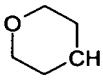
Comp. no.	R_1	R_2	X_1
A199	$CH(OCH_3)CH_2$	$CH_3OC(CH_3)_2$	O
A200	$CH(OCH_3)CH_2$	$HC{\equiv}CCH_2$	O
A201	$CH(OCH_3)CH_2$	$H_2C{=}CHCH_2$	O
A202	$CH(OCH_3)CH_2$	$CH_3C{\equiv}CCH_2$	O
A203	$CH(OCH_3)CH_2$		O
A204	$CH(OCH_3)CH_2$		O
A205	$CH(OCH_3)CH_2$		O
A206	$CH(OCH_3)CH_2$		O
A207	$CH(OCH_3)CH_2$		O
A208	$CH(OCH_3)CH_2$		O
A209	$CH(OCH_3)CH_2$		O
A210	$CH(OCH_3)CH_2$		O
A211	$CH(OCH_3)CH_2$		O
A212	$CH(OCH_3)CH_2$		O
A213	$CH(OCH_3)CH_2$		O
A214	$CH(OCH_3)CH_2$		O
A215	$CH(OCH_3)CH_2$		O
A216	$CH(OCH_3)CH_2$		O
A217	$CH(OCH_3)CH_2$		O

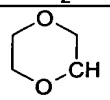
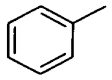
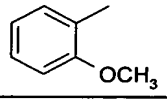
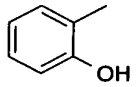
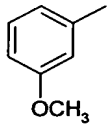
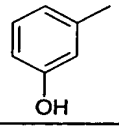
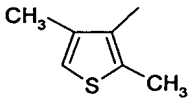
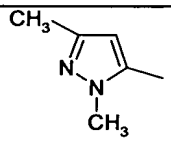
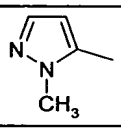
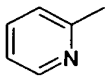
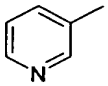
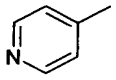
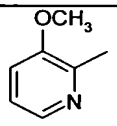
Comp. no.	R_1	R_2	X_1
A218	$CH(OCH_3)CH_2$		O
A219	$CH(OCH_3)CH_2$		O
A220	$CH(OCH_3)CH_2$		O
A221	$CH(OCH_3)CH_2$		O
A222	$CH(OCH_3)CH_2$		O
A223	$CH(OCH_3)CH_2$		O
A224	$CH(OCH_3)CH_2$		O
A225	$CH(OCH_3)CH_2$		O
A226	$CH(OCH_3)CH_2$		O
A227	$CH(OCH_3)CH_2$		O
A228	$CH(OCH_3)CH_2$		O
A229	$CH(OCH_3)CH_2$		O
A230	$CH(OCH_3)CH_2$		O

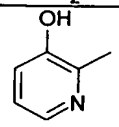
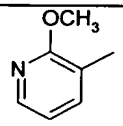
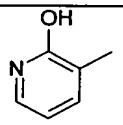
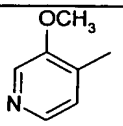
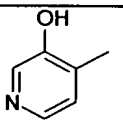
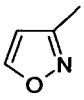
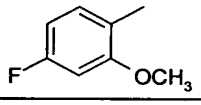
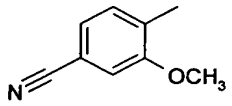
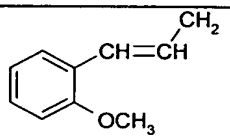
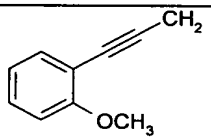
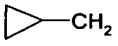
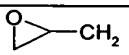
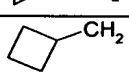
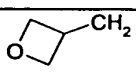
Comp. no.	R_1	R_2	X_1
A231	$CH(OCH_3)CH_2$		O
A232	$CH(OCH_3)CH_2$		O
A233	$CH(OCH_3)CH_2$		O
A234	$CH(OCH_3)CH_2$		O
A235	$CH(OCH_3)CH_2$		O
A236	$CH(OCH_3)CH_2$		O
A237	$CH(OCH_3)CH_2$		O
A238	$CH(OCH_3)CH_2$		O
A239	$CH(OCH_3)CH_2$		O
A240	$CH(OCH_3)CH_2$		O
A241	$CH(OCH_3)CH_2$		O
A242	$CH(OCH_3)CH_2$		O
A243	$CH(OCH_3)CH_2$		O
A244	$CH(OCH_3)CH_2$		O
A245	$CH(OCH_3)CH_2$		O
A246	$CH(OCH_3)CH_2$		O

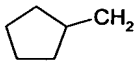
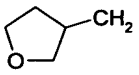
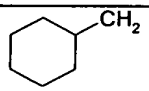
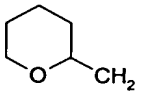
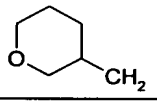
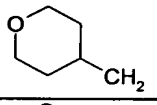
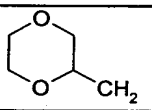
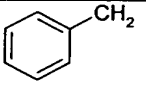
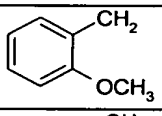
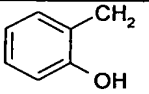
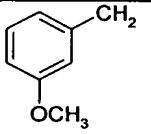
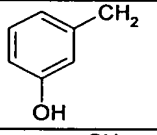
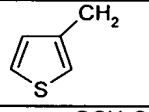
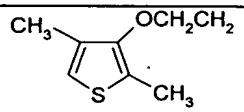
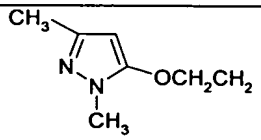
Comp. no.	R_1	R_2	X_1
A247	$CH(OCH_3)CH_2$		O
A248	$CH(OCH_3)CH_2$		O
A249	$CH(OCH_3)CH_2$		O
A250	$CH(OCH_3)CH_2$		O
A251	$CH(OCH_3)CH_2$		O
A252	$CH(OCH_3)CH_2$		O
A253	$CH(OCH_3)CH_2$		O
A254	$CH(OCH_3)CH_2$		O
A255	$CH(OCH_3)CH_2$		O
A256	$CH(OCH_3)CH_2$		O
A257	$CH(OCH_3)CH_2$		O
A258	$CH(OCH_3)CH_2$		O
A259	$CH(OCH_3)CH_2$		O
A260	$CH(OCH_3)CH_2$		O

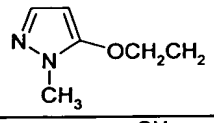
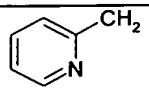
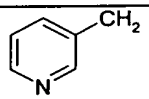
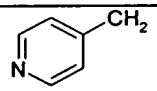
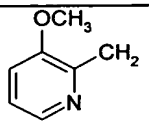
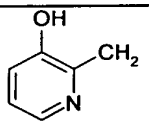
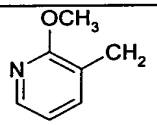
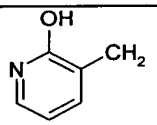
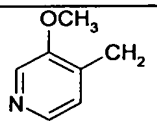
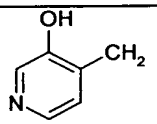
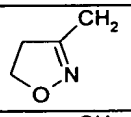
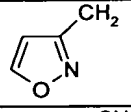
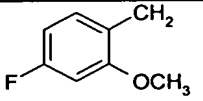
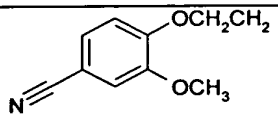
Comp. no.	R_1	R_2	X_1
A261	$CH(OCH_3)CH_2$		O
A262	$CH(OCH_3)CH_2$		O
A263	$CH(OCH_3)CH_2$		O
A264	$CH(OCH_3)CH_2$		O
A265	$CH(OCH_3)CH_2$		O
A266	$CH(OCH_3)CH_2$		O
A267	$CH(OCH_3)CH_2$		O
A268	$CH(OCH_3)CH_2$		O
A269	$CH(OCH_3)CH_2$		O
A270	$CH(OCH_3)CH_2$		O
A271	$CH(OCH_3)CH_2$		O
A272	$CH(OCH_3)CH_2$		O
A273	$CH_2CH(OCH_3)CH_2$	CH_3	O
A274	$CH_2CH(OCH_3)CH_2$	CH_3CH_2	O
A275	$CH_2CH(OCH_3)CH_2$	$(CH_3)_2CH$	O
A276	$CH_2CH(OCH_3)CH_2$	$PhCH_2$	O

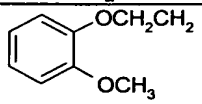
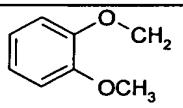
Comp. no.	R_1	R_2	X_1
A277	$CH_2CH(OCH_3)CH_2$	CH_3	S
A278	$CH_2CH(OCH_3)CH_2$	CH_3	SO
A279	$CH_2CH(OCH_3)CH_2$	CH_3	SO_2
A280	$CH_2CH(OCH_3)CH_2$	$CH_3CH_2CH_2$	O
A281	$CH_2CH(OCH_3)CH_2$	CH_3OCH_2	O
A282	$CH_2CH(OCH_3)CH_2$	$CH_3CH_2OCH_2$	O
A283	$CH_2CH(OCH_3)CH_2$	$CH_3OCH_2CH_2$	O
A284	$CH_2CH(OCH_3)CH_2$	$CH_3CH_2OCH_2CH_2$	O
A285	$CH_2CH(OCH_3)CH_2$	$CH_3OC(CH_3)_2CH_2$	O
A286	$CH_2CH(OCH_3)CH_2$	$CH_3OCH(CH_3)CH_2$	O
A287	$CH_2CH(OCH_3)CH_2$	$CH_3OCH_2CH(CH_3)$	O
A288	$CH_2CH(OCH_3)CH_2$	$CH_3OCH_2C(CH_3)_2$	O
A289	$CH_2CH(OCH_3)CH_2$	$CH_3OCH(CH_3)$	O
A290	$CH_2CH(OCH_3)CH_2$	$CH_3OC(CH_3)_2$	O
A291	$CH_2CH(OCH_3)CH_2$	$HC\equiv CCH_2$	O
A292	$CH_2CH(OCH_3)CH_2$	$H_2C=CHCH_2$	O
A293	$CH_2CH(OCH_3)CH_2$	$CH_3C\equiv CCH_2$	O
A294	$CH_2CH(OCH_3)CH_2$		O
A295	$CH_2CH(OCH_3)CH_2$		O
A296	$CH_2CH(OCH_3)CH_2$		O
A297	$CH_2CH(OCH_3)CH_2$		O
A298	$CH_2CH(OCH_3)CH_2$		O
A299	$CH_2CH(OCH_3)CH_2$		O
A300	$CH_2CH(OCH_3)CH_2$		O
A301	$CH_2CH(OCH_3)CH_2$		O
A302	$CH_2CH(OCH_3)CH_2$		O
A303	$CH_2CH(OCH_3)CH_2$		O

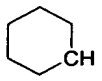
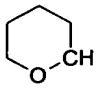
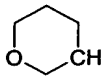
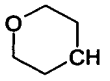
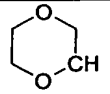
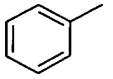
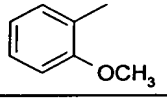
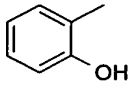
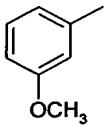
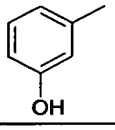
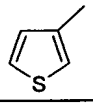
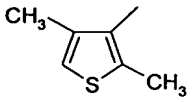
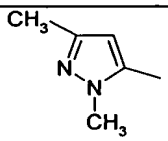
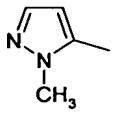
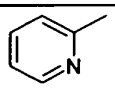
Comp. no.	R_1	R_2	X_1
A304	$CH_2CH(OCH_3)CH_2$		O
A305	$CH_2CH(OCH_3)CH_2$		O
A306	$CH_2CH(OCH_3)CH_2$		O
A307	$CH_2CH(OCH_3)CH_2$		O
A308	$CH_2CH(OCH_3)CH_2$		O
A309	$CH_2CH(OCH_3)CH_2$		O
A310	$CH_2CH(OCH_3)CH_2$		O
A311	$CH_2CH(OCH_3)CH_2$		O
A312	$CH_2CH(OCH_3)CH_2$		O
A313	$CH_2CH(OCH_3)CH_2$		O
A314	$CH_2CH(OCH_3)CH_2$		O
A315	$CH_2CH(OCH_3)CH_2$		O
A316	$CH_2CH(OCH_3)CH_2$		O
A317	$CH_2CH(OCH_3)CH_2$		O

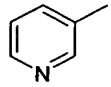
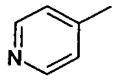
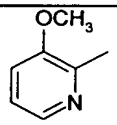
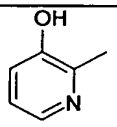
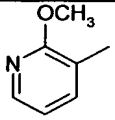
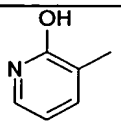
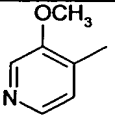
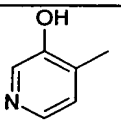
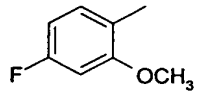
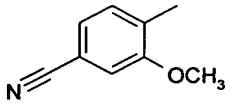
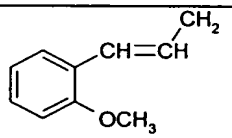
Comp. no.	R_1	R_2	X_1
A318	$CH_2CH(OCH_3)CH_2$		O
A319	$CH_2CH(OCH_3)CH_2$		O
A320	$CH_2CH(OCH_3)CH_2$		O
A321	$CH_2CH(OCH_3)CH_2$		O
A322	$CH_2CH(OCH_3)CH_2$		O
A323	$CH_2CH(OCH_3)CH_2$		O
A324	$CH_2CH(OCH_3)CH_2$		O
A325	$CH_2CH(OCH_3)CH_2$		O
A326	$CH_2CH(OCH_3)CH_2$		O
A327	$CH_2CH(OCH_3)CH_2$		O
A328	$CH_2CH(OCH_3)CH_2$		O
A329	$CH_2CH(OCH_3)CH_2$		O
A330	$CH_2CH(OCH_3)CH_2$		O
A331	$CH_2CH(OCH_3)CH_2$		O
A332	$CH_2CH(OCH_3)CH_2$		O

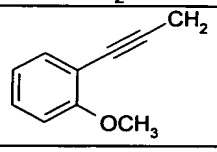
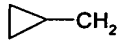
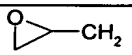
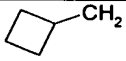
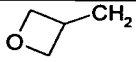
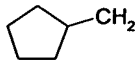
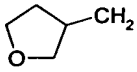
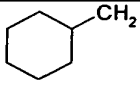
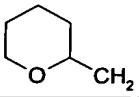
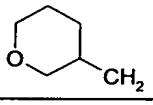
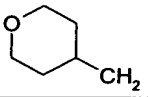
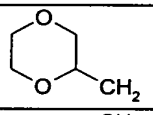
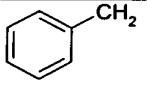
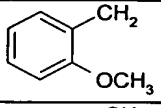
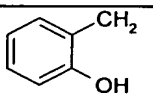
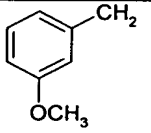
Comp. no.	R_1	R_2	X_1
A333	$CH_2CH(OCH_3)CH_2$		O
A334	$CH_2CH(OCH_3)CH_2$		O
A335	$CH_2CH(OCH_3)CH_2$		O
A336	$CH_2CH(OCH_3)CH_2$		O
A337	$CH_2CH(OCH_3)CH_2$		O
A338	$CH_2CH(OCH_3)CH_2$		O
A339	$CH_2CH(OCH_3)CH_2$		O
A340	$CH_2CH(OCH_3)CH_2$		O
A341	$CH_2CH(OCH_3)CH_2$		O
A342	$CH_2CH(OCH_3)CH_2$		O
A343	$CH_2CH(OCH_3)CH_2$		O
A344	$CH_2CH(OCH_3)CH_2$		O
A345	$CH_2CH(OCH_3)CH_2$		O
A346	$CH_2CH(OCH_3)CH_2$		O
A347	$CH_2CH(OCH_3)CH_2$		O

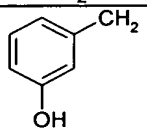
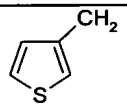
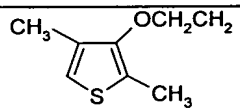
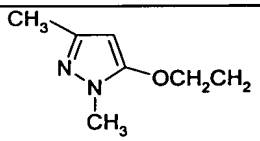
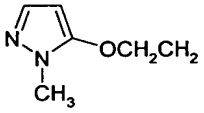
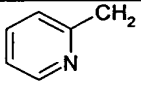
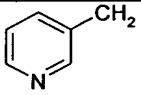
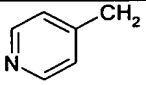
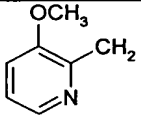
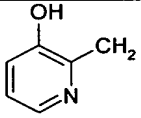
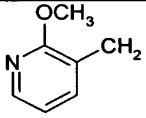
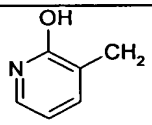
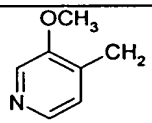
Comp. no.	R_1	R_2	X_1
A348	$CH_2CH(OCH_3)CH_2$		O
A349	$CH_2CH(OCH_3)CH_2$		O
A350	$CH_2CH(OCH_3)CH_2$		O
A351	$CH_2CH(OCH_3)CH_2$		O
A352	$CH_2CH(OCH_3)CH_2$		O
A353	$CH_2CH(OCH_3)CH_2$		O
A354	$CH_2CH(OCH_3)CH_2$		O
A355	$CH_2CH(OCH_3)CH_2$		O
A356	$CH_2CH(OCH_3)CH_2$		O
A357	$CH_2CH(OCH_3)CH_2$		O
A358	$CH_2CH(OCH_3)CH_2$		O
A359	$CH_2CH(OCH_3)CH_2$		O
A360	$CH_2CH(OCH_3)CH_2$		O
A361	$CH_2CH(OCH_3)CH_2$		O

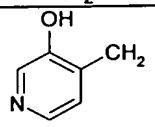
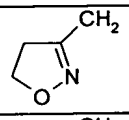
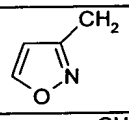
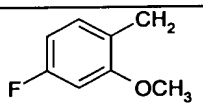
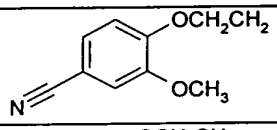
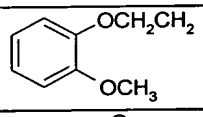
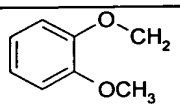
Comp. no.	R_1	R_2	X_1
A362	$CH_2CH(OCH_3)CH_2$		O
A363	$CH_2CH(OCH_3)CH_2$		O
A364	$CH=CHCH_2$	CH_3	O
A365	$CH=CHCH_2$	CH_3CH_2	O
A366	$CH=CHCH_2$	$(CH_3)_2CH$	O
A367	$CH=CHCH_2$	$PhCH_2$	O
A368	$CH=CHCH_2$	CH_3	S
A369	$CH=CHCH_2$	CH_3	SO
A370	$CH=CHCH_2$	CH_3	SO_2
A371	$CH=CHCH_2$	$CH_3CH_2CH_2$	O
A372	$CH=CHCH_2$	CH_3OCH_2	O
A373	$CH=CHCH_2$	$CH_3CH_2OCH_2$	O
A374	$CH=CHCH_2$	$CH_3OCH_2CH_2$	O
A375	$CH=CHCH_2$	$CH_3CH_2OCH_2CH_2$	O
A376	$CH=CHCH_2$	$CH_3OC(CH_3)_2CH_2$	O
A377	$CH=CHCH_2$	$CH_3OCH(CH_3)CH_2$	O
A378	$CH=CHCH_2$	$CH_3OCH_2CH(CH_3)$	O
A379	$CH=CHCH_2$	$CH_3OCH_2C(CH_3)_2$	O
A380	$CH=CHCH_2$	$CH_3OCH(CH_3)$	O
A381	$CH=CHCH_2$	$CH_3OC(CH_3)_2$	O
A382	$CH=CHCH_2$	$HC\equiv CCH_2$	O
A383	$CH=CHCH_2$	$H_2C=CHCH_2$	O
A384	$CH=CHCH_2$	$CH_3C\equiv CCH_2$	O
A385	$CH=CHCH_2$		O
A386	$CH=CHCH_2$		O
A387	$CH=CHCH_2$		O
A388	$CH=CHCH_2$		O
A389	$CH=CHCH_2$		O
A390	$CH=CHCH_2$		O

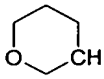
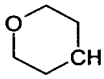
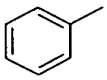
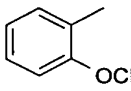
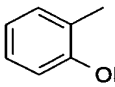
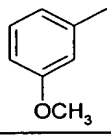
Comp. no.	R_1	R_2	X_1
A391	$CH=CHCH_2$		O
A392	$CH=CHCH_2$		O
A393	$CH=CHCH_2$		O
A394	$CH=CHCH_2$		O
A395	$CH=CHCH_2$		O
A396	$CH=CHCH_2$		O
A397	$CH=CHCH_2$		O
A398	$CH=CHCH_2$		O
A399	$CH=CHCH_2$		O
A400	$CH=CHCH_2$		O
A401	$CH=CHCH_2$		O
A402	$CH=CHCH_2$		O
A403	$CH=CHCH_2$		O
A404	$CH=CHCH_2$		O
A405	$CH=CHCH_2$		O

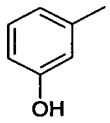
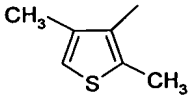
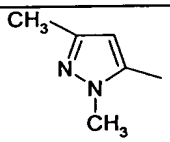
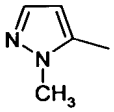
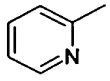
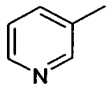
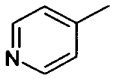
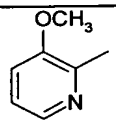
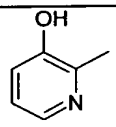
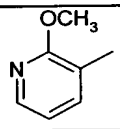
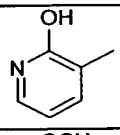
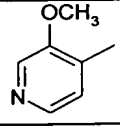
Comp. no.	R_1	R_2	X_1
A406	$CH=CHCH_2$		O
A407	$CH=CHCH_2$		O
A408	$CH=CHCH_2$		O
A409	$CH=CHCH_2$		O
A410	$CH=CHCH_2$		O
A411	$CH=CHCH_2$		O
A412	$CH=CHCH_2$		O
A413	$CH=CHCH_2$		O
A414	$CH=CHCH_2$		O
A415	$CH=CHCH_2$		O
A416	$CH=CHCH_2$		O
A417	$CH=CHCH_2$		O
A418	$CH=CHCH_2$		O

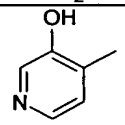
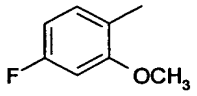
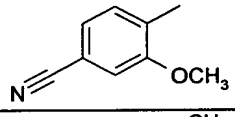
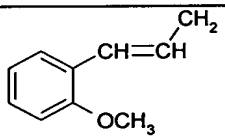
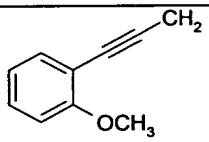
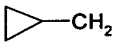
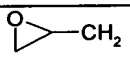
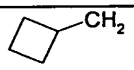
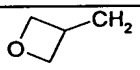
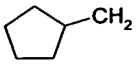
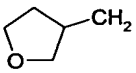
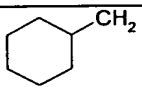
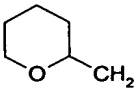
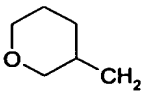
Comp. no.	R_1	R_2	X_1
A419	$CH=CHCH_2$		O
A420	$CH=CHCH_2$		O
A421	$CH=CHCH_2$		O
A422	$CH=CHCH_2$		O
A423	$CH=CHCH_2$		O
A424	$CH=CHCH_2$		O
A425	$CH=CHCH_2$		O
A426	$CH=CHCH_2$		O
A427	$CH=CHCH_2$		O
A428	$CH=CHCH_2$		O
A429	$CH=CHCH_2$		O
A430	$CH=CHCH_2$		O
A431	$CH=CHCH_2$		O
A432	$CH=CHCH_2$		O
A433	$CH=CHCH_2$		O
A434	$CH=CHCH_2$		O

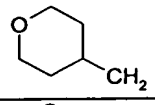
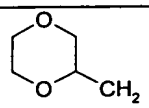
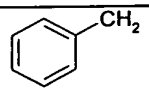
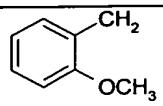
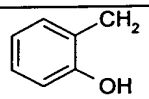
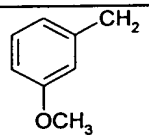
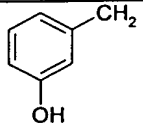
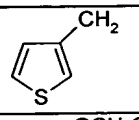
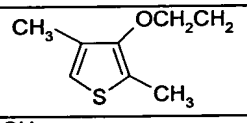
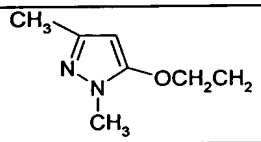
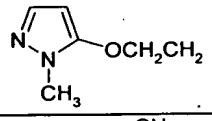
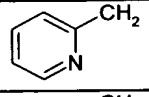
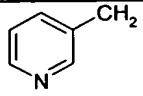
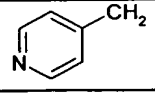
Comp. no.	R_1	R_2	X_1
A435	$CH=CHCH_2$		O
A436	$CH=CHCH_2$		O
A437	$CH=CHCH_2$		O
A438	$CH=CHCH_2$		O
A439	$CH=CHCH_2$		O
A440	$CH=CHCH_2$		O
A441	$CH=CHCH_2$		O
A442	$CH=CHCH_2$		O
A443	$CH=CHCH_2$		O
A444	$CH=CHCH_2$		O
A445	$CH=CHCH_2$		O
A446	$CH=CHCH_2$		O
A447	$CH=CHCH_2$		O

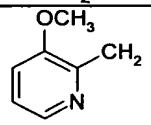
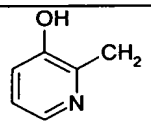
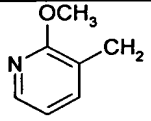
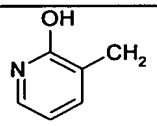
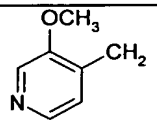
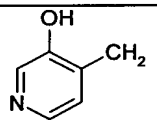
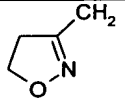
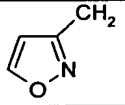
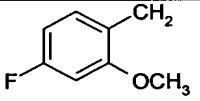
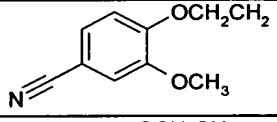
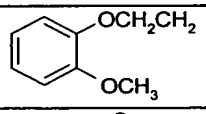
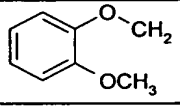
Comp. no.	R_1	R_2	X_1
A448	$CH=CHCH_2$		O
A449	$CH=CHCH_2$		O
A450	$CH=CHCH_2$		O
A451	$CH=CHCH_2$		O
A452	$CH=CHCH_2$		O
A453	$CH=CHCH_2$		O
A454	$CH=CHCH_2$		O
A455	$C\equiv CCH_2$	CH_3	O
A456	$C\equiv CCH_2$	CH_3CH_2	O
A457	$C\equiv CCH_2$	$(CH_3)_2CH$	O
A458	$C\equiv CCH_2$	$PhCH_2$	O
A459	$C\equiv CCH_2$	CH_3	S
A460	$C\equiv CCH_2$	CH_3	SO
A461	$C\equiv CCH_2$	CH_3	SO_2
A462	$C\equiv CCH_2$	$CH_3CH_2CH_2$	O
A463	$C\equiv CCH_2$	CH_3OCH_2	O
A464	$C\equiv CCH_2$	$CH_3CH_2OCH_2$	O
A465	$C\equiv CCH_2$	$CH_3OCH_2CH_2$	O
A466	$C\equiv CCH_2$	$CH_3CH_2OCH_2CH_2$	O
A467	$C\equiv CCH_2$	$CH_3OC(CH_3)_2CH_2$	O
A468	$C\equiv CCH_2$	$CH_3OCH(CH_3)CH_2$	O
A469	$C\equiv CCH_2$	$CH_3OCH_2CH(CH_3)$	O
A470	$C\equiv CCH_2$	$CH_3OCH_2C(CH_3)_2$	O
A471	$C\equiv CCH_2$	$CH_3OCH(CH_3)$	O

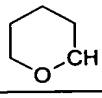
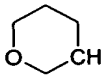
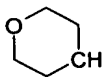
Comp. no.	R_1	R_2	X_1
A472	$C\equiv CCH_2$	$CH_3OC(CH_3)_2$	O
A473	$C\equiv CCH_2$	$HC\equiv CCH_2$	O
A474	$C\equiv CCH_2$	$H_2C=CHCH_2$	O
A475	$C\equiv CCH_2$	$CH_3C\equiv CCH_2$	O
A476	$C\equiv CCH_2$		O
A477	$C\equiv CCH_2$		O
A478	$C\equiv CCH_2$		O
A479	$C\equiv CCH_2$		O
A480	$C\equiv CCH_2$		O
A481	$C\equiv CCH_2$		O
A482	$C\equiv CCH_2$		O
A483	$C\equiv CCH_2$		O
A484	$C\equiv CCH_2$		O
A485	$C\equiv CCH_2$		O
A486	$C\equiv CCH_2$		O
A487	$C\equiv CCH_2$		O
A488	$C\equiv CCH_2$		O
A489	$C\equiv CCH_2$		O
A490	$C\equiv CCH_2$		O

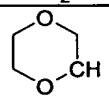
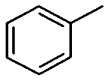
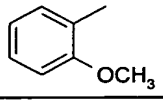
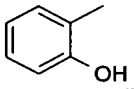
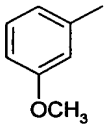
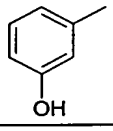
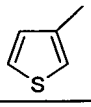
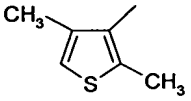
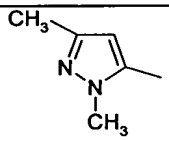
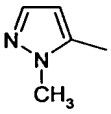
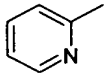
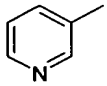
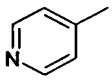
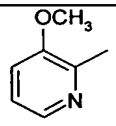
Comp. no.	R_1	R_2	X_1
A491	$C\equiv CCH_2$		O
A492	$C\equiv CCH_2$		O
A493	$C\equiv CCH_2$		O
A494	$C\equiv CCH_2$		O
A495	$C\equiv CCH_2$		O
A496	$C\equiv CCH_2$		O
A497	$C\equiv CCH_2$		O
A498	$C\equiv CCH_2$		O
A499	$C\equiv CCH_2$		O
A500	$C\equiv CCH_2$		O
A501	$C\equiv CCH_2$		O
A502	$C\equiv CCH_2$		O
A503	$C\equiv CCH_2$		O

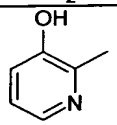
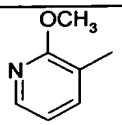
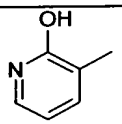
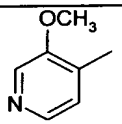
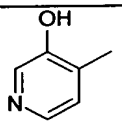
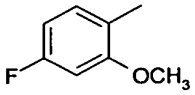
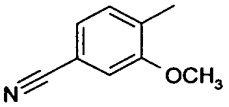
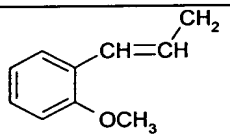
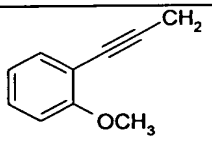
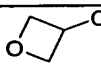
Comp. no.	R_1	R_2	X_1
A504	$C\equiv CCH_2$		O
A505	$C\equiv CCH_2$		O
A506	$C\equiv CCH_2$		O
A507	$C\equiv CCH_2$		O
A508	$C\equiv CCH_2$		O
A509	$C\equiv CCH_2$		O
A510	$C\equiv CCH_2$		O
A511	$C\equiv CCH_2$		O
A512	$C\equiv CCH_2$		O
A513	$C\equiv CCH_2$		O
A514	$C\equiv CCH_2$		O
A515	$C\equiv CCH_2$		O
A516	$C\equiv CCH_2$		O
A517	$C\equiv CCH_2$		O
A518	$C\equiv CCH_2$		O
A519	$C\equiv CCH_2$		O

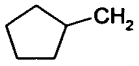
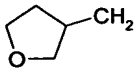
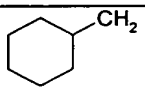
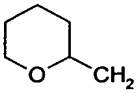
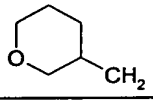
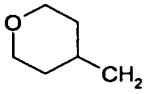
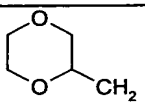
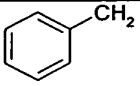
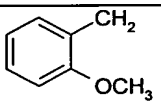
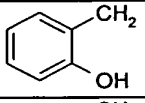
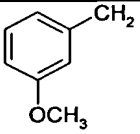
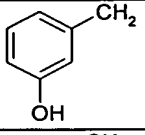
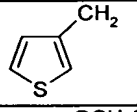
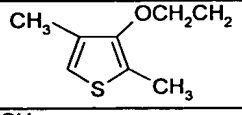
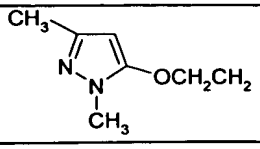
Comp. no.	R_1	R_2	X_1
A520	$C\equiv CCH_2$		O
A521	$C\equiv CCH_2$		O
A522	$C\equiv CCH_2$		O
A523	$C\equiv CCH_2$		O
A524	$C\equiv CCH_2$		O
A525	$C\equiv CCH_2$		O
A526	$C\equiv CCH_2$		O
A527	$C\equiv CCH_2$		O
A528	$C\equiv CCH_2$		O
A529	$C\equiv CCH_2$		O
A530	$C\equiv CCH_2$		O
A531	$C\equiv CCH_2$		O
A532	$C\equiv CCH_2$		O
A533	$C\equiv CCH_2$		O

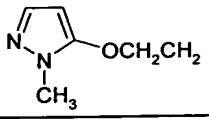
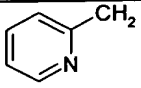
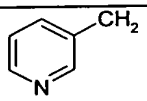
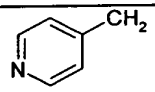
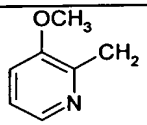
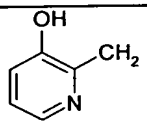
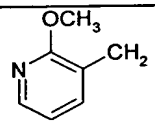
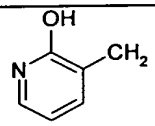
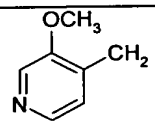
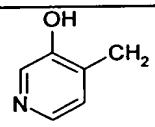
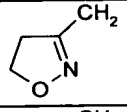
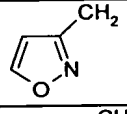
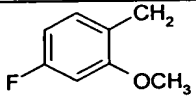
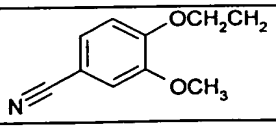
Comp. no.	R_1	R_2	X_1
A534	$C\equiv CCH_2$		O
A535	$C\equiv CCH_2$		O
A536	$C\equiv CCH_2$		O
A537	$C\equiv CCH_2$		O
A538	$C\equiv CCH_2$		O
A539	$C\equiv CCH_2$		O
A540	$C\equiv CCH_2$		O
A541	$C\equiv CCH_2$		O
A542	$C\equiv CCH_2$		O
A543	$C\equiv CCH_2$		O
A544	$C\equiv CCH_2$		O
A545	$C\equiv CCH_2$		O
A546	CH_2	CH_3	O
A547	CH_2	CH_3CH_2	O
A548	CH_2	$(CH_3)_2CH$	O
A549	CH_2	$PhCH_2$	O

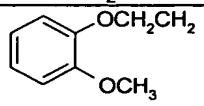
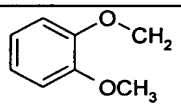
Comp. no.	R_1	R_2	X_1
A550	CH_2	CH_3	S
A551	CH_2	CH_3	SO
A552	CH_2	CH_3	SO_2
A553	CH_2	$CH_3CH_2CH_2$	O
A554	CH_2	CH_3OCH_2	O
A555	CH_2	$CH_3CH_2OCH_2$	O
A556	CH_2	$CH_3OCH_2CH_2$	O
A557	CH_2	$CH_3CH_2OCH_2CH_2$	O
A558	CH_2	$CH_3OC(CH_3)_2CH_2$	O
A559	CH_2	$CH_3OCH(CH_3)CH_2$	O
A560	CH_2	$CH_3OCH_2CH(CH_3)$	O
A561	CH_2	$CH_3OCH_2C(CH_3)_2$	O
A562	CH_2	$CH_3OCH(CH_3)$	O
A563	CH_2	$CH_3OC(CH_3)_2$	O
A564	CH_2	$HC\equiv CCH_2$	O
A565	CH_2	$H_2C=CHCH_2$	O
A566	CH_2	$CH_3C\equiv CCH_2$	O
A567	CH_2		O
A568	CH_2		O
A569	CH_2		O
A570	CH_2		O
A571	CH_2		O
A572	CH_2		O
A573	CH_2		O
A574	CH_2		O
A575	CH_2		O
A576	CH_2		O

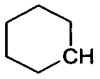
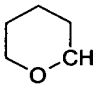
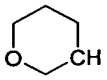
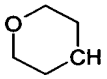
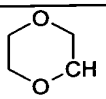
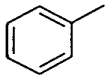
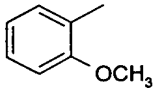
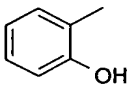
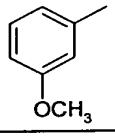
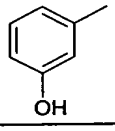
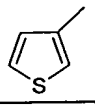
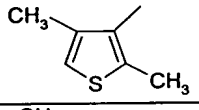
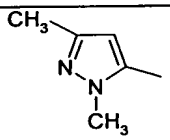
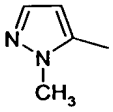
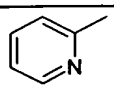
Comp. no.	R_1	R_2	X_1
A577	CH_2		O
A578	CH_2		O
A579	CH_2		O
A580	CH_2		O
A581	CH_2		O
A582	CH_2		O
A583	CH_2		O
A584	CH_2		O
A585	CH_2		O
A586	CH_2		O
A587	CH_2		O
A588	CH_2		O
A589	CH_2		O
A590	CH_2		O

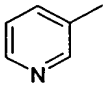
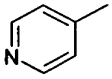
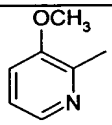
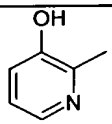
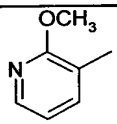
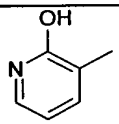
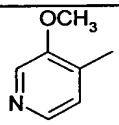
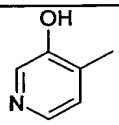
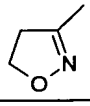
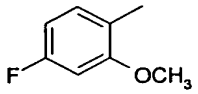
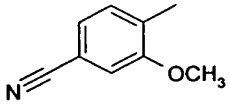
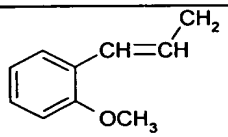
Comp. no.	R_1	R_2	X_1
A591	CH_2		O
A592	CH_2		O
A593	CH_2		O
A594	CH_2		O
A595	CH_2		O
A596	CH_2		O
A597	CH_2		O
A598	CH_2		O
A599	CH_2		O
A600	CH_2		O
A601	CH_2		O
A602	CH_2		O
A603	CH_2		O
A604	CH_2		O
A605	CH_2		O

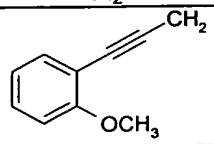
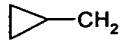
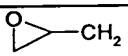
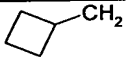
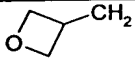
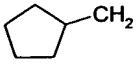
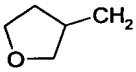
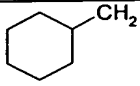
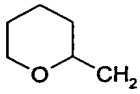
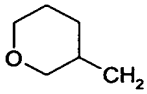
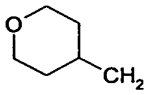
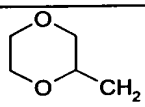
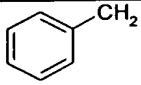
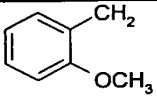
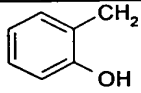
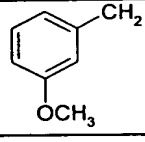
Comp. no.	R_1	R_2	X_1
A606	CH_2		O
A607	CH_2		O
A608	CH_2		O
A609	CH_2		O
A610	CH_2		O
A611	CH_2		O
A612	CH_2		O
A613	CH_2		O
A614	CH_2		O
A615	CH_2		O
A616	CH_2		O
A617	CH_2		O
A618	CH_2		O
A619	CH_2		O
A620	CH_2		O

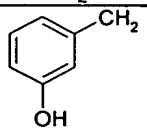
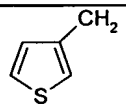
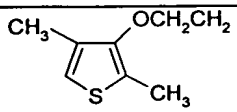
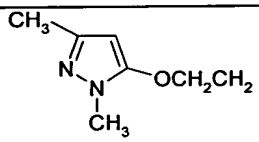
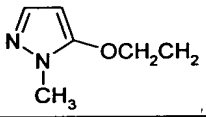
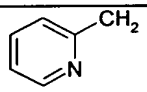
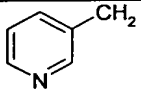
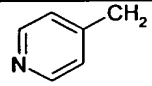
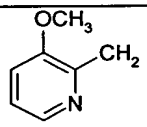
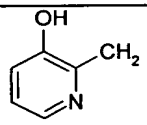
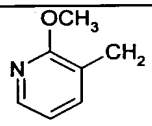
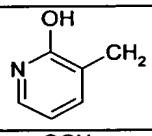
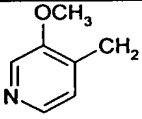
Comp. no.	R_1	R_2	X_1
A621	CH_2		O
A622	CH_2		O
A623	CH_2		O
A624	CH_2		O
A625	CH_2		O
A626	CH_2		O
A627	CH_2		O
A628	CH_2		O
A629	CH_2		O
A630	CH_2		O
A631	CH_2		O
A632	CH_2		O
A633	CH_2		O
A634	CH_2		O

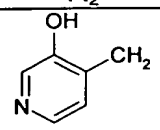
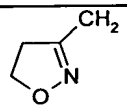
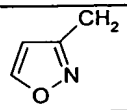
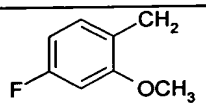
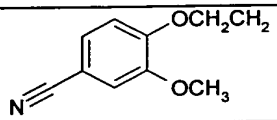
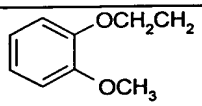
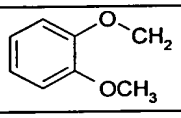
Comp. no.	R_1	R_2	X_1
A635	CH_2		O
A636	CH_2		O
A637	CH_2	CH_3	O
A638	CH_2	CH_2CH_3	O
A639	CH_2	$(CH_3)_2CH$	O
A640	CH_2	$PhCH_2$	O
A641	CH_2	CH_3	S
A642	CH_2	CH_3	O
A643	CH_2	CH_3	O
A644	CH_2	CH_3OCH_2	O
A645	CH_2	$CH_3CH_2OCH_2$	O
A646	CH_2	$CH_3OCH_2CH_2$	O
A647	CH_2	$CH_3CH_2OCH_2CH_2$	O
A648	CH_2	$CH_3OC(CH_3)_2CH_2$	O
A649	CH_2	$CH_3OCH(CH_3)CH_2$	O
A650	CH_2	$CH_3OCH_2CH(CH_3)$	O
A651	CH_2	$CH_3OCH_2C(CH_3)_2$	O
A652	CH_2	$CH_3OCH(CH_3)$	O
A653	CH_2	$CH_3OC(CH_3)_2$	O
A654	CH_2	$HC\equiv CCH_2$	O
A655	CH_2	$H_2C=CHCH_2$	O
A656	CH_2	$CH_3C\equiv CCH_2$	O
A657	CH_2		O
A658	CH_2		O
A659	CH_2		O
A660	CH_2		O
A661	CH_2		O
A662	CH_2		O

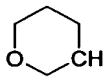
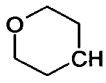
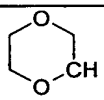
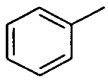
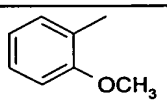
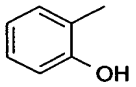
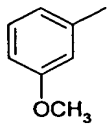
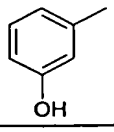
Comp. no.	R_1	R_2	X_1
A663	CH_2		O
A664	CH_2		O
A665	CH_2		O
A666	CH_2		O
A667	CH_2		O
A668	CH_2		O
A669	CH_2		O
A670	CH_2		O
A671	CH_2		O
A672	CH_2		O
A673	CH_2		O
A674	CH_2		O
A675	CH_2		O
A676	CH_2		O
A677	CH_2		O

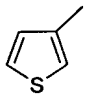
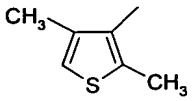
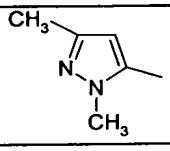
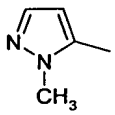
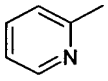
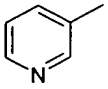
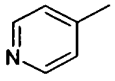
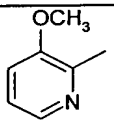
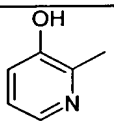
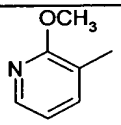
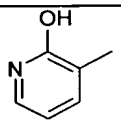
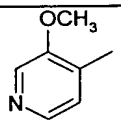
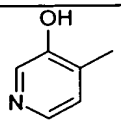
Comp. no.	R_1	R_2	X_1
A678	CH_2		O
A679	CH_2		O
A680	CH_2		O
A681	CH_2		O
A682	CH_2		S
A683	CH_2		SO
A684	CH_2		SO_2
A685	CH_2		O
A686	CH_2		O
A687	CH_2		O
A688	CH_2		O
A689	CH_2		O
A690	CH_2		O

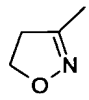
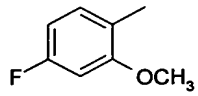
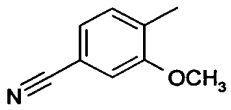
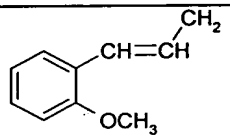
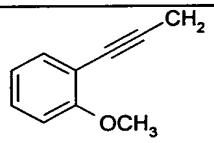
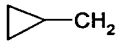
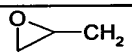
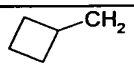
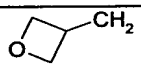
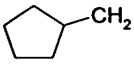
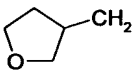
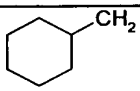
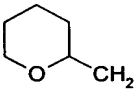
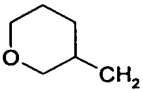
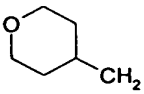
Comp. no.	R_1	R_2	X_1
A691	CH_2		O
A692	CH_2		O
A693	CH_2		O
A694	CH_2		O
A695	CH_2		O
A696	CH_2		O
A697	CH_2		O
A698	CH_2		O
A699	CH_2		O
A700	CH_2		O
A701	CH_2		O
A702	CH_2		O
A703	CH_2		O
A704	CH_2		O
A705	CH_2		O
A706	CH_2		O

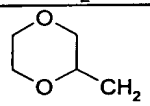
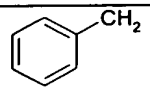
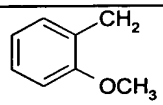
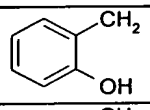
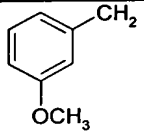
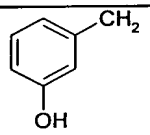
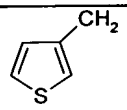
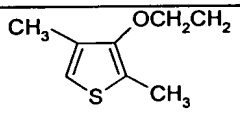
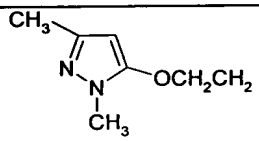
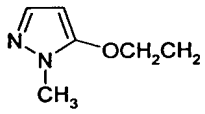
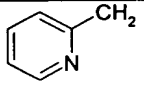
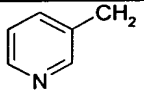
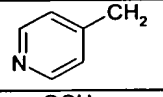
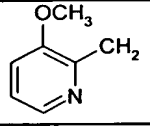
Comp. no.	R_1	R_2	X_1
A707	CH_2		O
A708	CH_2		O
A709	CH_2		O
A710	CH_2		O
A711	CH_2		O
A712	CH_2		O
A713	CH_2		O
A714	CH_2		O
A715	CH_2		O
A716	CH_2		O
A717	CH_2		O
A718	CH_2		O
A719	CH_2		O

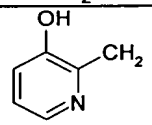
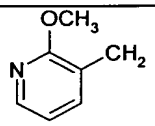
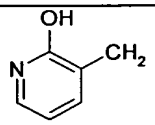
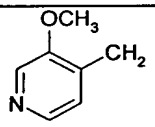
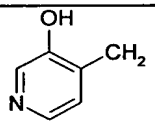
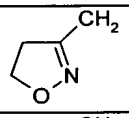
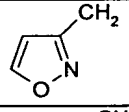
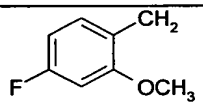
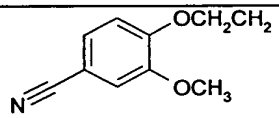
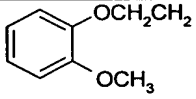
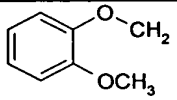
Comp. no.	R_1	R_2	X_1
A720	CH_2		O
A721	CH_2		O
A722	CH_2		O
A723	CH_2		O
A724	CH_2		O
A725	CH_2		O
A726	CH_2		O
A727	CH_2	CH_3	O
A728	CH_2	CH_2CH_3	O
A729	CH_2	$(CH_3)_2CH$	O
A730	CH_2	$PhCH_2$	O
A731	CH_2	CH_3	S
A732	CH_2	CH_3	SO
A733	CH_2	CH_3	SO_2
A734	CH_2	CH_3OCH_2	O
A735	CH_2	$CH_3CH_2OCH_2$	O
A736	CH_2	$CH_3OCH_2CH_2$	O
A737	CH_2	$CH_3CH_2OCH_2CH_2$	O
A738	CH_2	$CH_3OC(CH_3)_2CH_2$	O
A739	CH_2	$CH_3OCH(CH_3)CH_2$	O
A740	CH_2	$CH_3OCH_2CH(CH_3)$	O
A741	CH_2	$CH_3OCH_2C(CH_3)_2$	O
A742	CH_2	$CH_3OCH(CH_3)$	O
A743	CH_2	$CH_3OC(CH_3)_2$	O

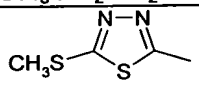
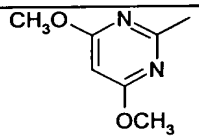
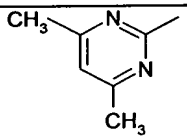
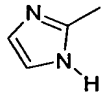
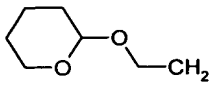
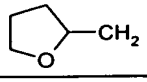
Comp. no.	R_1	R_2	X_1
A744	CH_2	$HC{\equiv}CCH_2$	O
A745	CH_2	$H_2C{=}CHCH_2$	O
A746	CH_2	$CH_3C{\equiv}CCH_2$	O
A747	CH_2		O
A748	CH_2		O
A749	CH_2		O
A750	CH_2		O
A751	CH_2		O
A752	CH_2		O
A753	CH_2		O
A754	CH_2		O
A755	CH_2		O
A756	CH_2		O
A757	CH_2		O
A758	CH_2		O
A759	CH_2		O
A760	CH_2		O
A761	CH_2		O
A762	CH_2		O

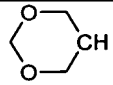
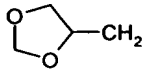
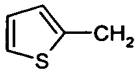
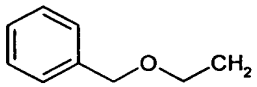
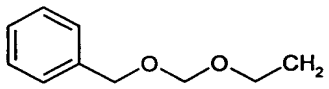
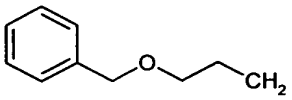
Comp. no.	R_1	R_2	X_1
A763	CH_2		O
A764	CH_2		O
A765	CH_2		O
A766	CH_2		O
A767	CH_2		O
A768	CH_2		O
A769	CH_2		O
A770	CH_2		O
A771	CH_2		O
A772	CH_2		O
A773	CH_2		O
A774	CH_2		O
A775	CH_2		O

Comp. no.	R_1	R_2	X_1
A776	CH_2		O
A777	CH_2		O
A778	CH_2		O
A779	CH_2		O
A780	CH_2		O
A781	CH_2		O
A782	CH_2		O
A783	CH_2		O
A784	CH_2		O
A785	CH_2		O
A786	CH_2		O
A787	CH_2		O
A788	CH_2		O
A789	CH_2		O
A790	CH_2		O
A791	CH_2		O

Comp. no.	R_1	R_2	X_1
A792	CH_2		O
A793	CH_2		O
A794	CH_2		O
A795	CH_2		O
A796	CH_2		O
A797	CH_2		O
A798	CH_2		O
A799	CH_2		O
A800	CH_2		O
A801	CH_2		O
A802	CH_2		O
A803	CH_2		O
A804	CH_2		O
A805	CH_2		O

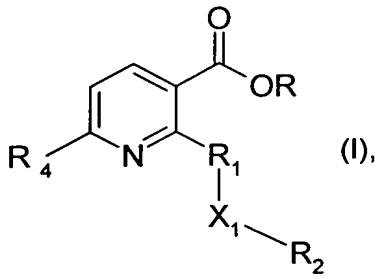
Comp. no.	R_1	R_2	X_1
A806	CH_2		O
A807	CH_2		O
A808	CH_2		O
A809	CH_2		O
A810	CH_2		O
A811	CH_2		O
A812	CH_2		O
A813	CH_2		O
A814	CH_2		O
A815	CH_2		O
A816	CH_2		O
A817	CH_2	$CH_3SCH_2CH_2$	O
A818	CH_2	$CH_3SOCH_2CH_2$	O
A819	CH_2	$CH_3SO_2CH_2CH_2$	O
A820	CH_2	$CH_3OCH_2CH_2$	O
A821	CH_2	$CH_3OCH_2CH_2$	O
A822	CH_2	$CH_3OCH_2CH_2$	O
A823	CH_2	$CH_3OCH_2CH_2$	O

Comp. no.	R_1	R_2	X_1
A824	CH_2	$CH_3OCH_2CH_2$	O
A825	CH_2	$CH_3OCH_2CH_2$	S
A826	CH_2	$CH_3OCH_2CH_2$	SO
A827	CH_2	$CH_3OCH_2CH_2$	SO_2
A828	CH_2	$CH_3SO_2CH_2CH_2$	O
A829	CH_2		S
A830	CH_2		S
A831	CH_2		S
A832	CH_2		S
A833	CH_2	$CH_3C(O)$	O
A834	CH_2	CF_3CH_2	O
A835	CH_2	$CH_3OCH_2CH_2OCH_2CH_2$	O
A836	CH_2	$HC{\equiv}CCH_2CH_2$	O
A837	CH_2		O
A838	CH_2	$CH_3CH_2C(OCH_3)HOCH_2CH_2$	O
A839	CH_2	$(CH_3)_3CC(O)$	O
A840	CH_2	$CH_2{=}CHCH_2OCH_2CH_2$	O
A841	CH_2	$CH_3CH_2CH_2OCH_2CH_2$	O
A842	CH_2		O
A843	CH_2	n-heptyl-C(O)	O
A844	CH_2	phenyl-C(O)	O
A845	CH_2	$CF_3CH_2OCH_2CH_2$	O
A846	CH_2	$CH_3OCH_2CH_2CH_2$	O
A847	CH_2	$HOCH_2CH_2CH_2$	O
A848	CH_2		O

Comp. no.	R_1	R_2	X_1
A849	CH_2	$N{\equiv}CCH_2CH_2$	O
A850	CH_2	$ClCH_2CH_2$	O
A851	CH_2		O
A852	CH_2		O
A853	CH_2	$CH_3OCH_2C(Br)HCH_2$	O
A854	CH_2		O
A855	CH_2		O
A856	CH_2	$HOCH_2CH_2$	O
A857	CH_2		O
A858	CH_2	$CH_3(OCH_2CH_2)_3$	O
A859	CH_2	$CH_3CH_2OC(CH_3)HOCH_2CH_2$	O
A860	CH_2	n-heptyl-$C(O)OCH_2CH_2$	O
A861	CH_2	$CH_3C(O)OCH_2CH_2$	O
A862	CH_2	$CH_3SO_2OCH_2CH_2$	O
A863	CH_2		O
A864	CH_2	CH_3	$-N(CH_3)SO_2-$
A865	CH_2	$HOCH_2C(OH)HCH_2$	O
A866	CH_2	phenyl-$C(O)OCH_2CH_2$	O
A867	CH_2	tert-butyl-$C(O)OCH_2CH_2$	O
A868	CH_2	$CH_3OC(O)CH_2$	O

Patent claims:

1. A process for the preparation of a compound of formula I



(I),

wherein

R is C_1-C_6alkyl;

R_1 is a C_1-C_6alkylene, C_3-C_6alkenylene or C_3-C_6alkynylene chain which may be substituted one or more times by halogen or by R_5, the unsaturated bonds of the chain not being attached directly to the substituent X_1;

R_4 is halomethyl or haloethyl;

X_1 is oxygen, -O(CO)-, -(CO)O-, -O(CO)O-, -N(R_6)-O-, -O-NR_{17}-, thio, sulfinyl, sulfonyl, -SO_2NR_7-, -$NR_{18}SO_2$- or -NR_8-;

R_2 is hydrogen or C_1-C_8alkyl, or is a C_1-C_8alkyl, C_3-C_6alkenyl or C_3-C_6alkynyl group which may be substituted one or more times by halogen, hydroxy, amino, formyl, nitro, cyano, mercapto, carbamoyl, C_1-C_6alkoxy, C_1-C_6alkoxycarbonyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl, halo-substituted C_3-C_6cycloalkyl, or by C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, C_1-C_6haloalkoxy, C_3-C_6haloalkenyloxy, cyano-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkylthio-C_1-C_6alkoxy, C_1-C_6alkylsulfinyl-C_1-C_6alkoxy, C_1-C_6alkylsulfonyl-C_1-C_6alkoxy, C_1-C_6alkoxycarbonyl-C_1-C_6alkoxy, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbonyl, C_1-C_6alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylthio, C_1-C_6haloalkylsulfinyl, C_1-C_6haloalkylsulfonyl, oxiranyl (which may in turn be substituted by C_1-C_6alkyl), or by (3-oxetanyl)oxy (which may in turn be substituted by C_1-C_6alkyl), or by benzylthio, benzylsulfinyl, benzylsulfonyl, C_1-C_6alkylamino, di(C_1-C_6alkyl)amino, $R_9S(O)_2O$, $R_{10}N(R_{11})SO_2$-, rhodano, phenyl, phenoxy, phenylthio, phenylsulfinyl or by phenylsulfonyl; it being possible for the phenyl- or benzyl-containing groups to be in turn substituted by one or more C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, halogen, cyano, hydroxy or nitro groups, or

R_2 is phenyl which may be substituted one or more times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, halogen, cyano, hydroxy or by nitro; or
R_2 is C_3-C_6cycloalkyl, C_1-C_6alkoxy- or C_1-C_6alkyl-substituted C_3-C_6cycloalkyl, 3-oxetanyl or C_1-C_6alkyl-substituted 3-oxetanyl; or
R_2 is a five- to ten-membered, monocyclic or fused bicyclic, ring system which may be aromatic, partially saturated or fully saturated and may contain from 1 to 4 hetero atoms selected from nitrogen, oxygen, sulfur, or may contain the group C=O or C=NR_{19}, the ring system being attached to the substituent X_1 directly or by way of a C_1-C_4alkylene, C_2-C_4alkenyl-C_1-C_4alkylene, C_2-C_4alkynyl-C_1-C_4alkylene, -N(R_{12})-C_1-C_4alkylene, -SO-C_1-C_4alkylene or -SO_2-C_1-C_4alkylene group and each ring system containing no more than 2 oxygen atoms and no more than two sulfur atoms, and it being possible for each ring system itself to be substituted one or more times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6alkynyl, C_2-C_6haloalkynyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, mercapto, amino, hydroxy, C_1-C_6alkylthio, C_1-C_6haloalkylthio, C_3-C_6alkenylthio, C_3-C_6haloalkenylthio, C_3-C_6alkynylthio, C_1-C_3alkoxy-C_1-C_3alkylthio, C_1-C_4alkylcarbonyl-C_1-C_3alkylthio, C_1-C_4alkoxycarbonyl-C_1-C_3alkylthio, cyano-C_1-C_3alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylsulfonyl, aminosulfonyl, C_1-C_2alkylaminosulfonyl, N,N-di(C_1-C_2alkyl)aminosulfonyl, di(C_1-C_4alkyl)amino, halogen, cyano, nitro or by phenyl, it being possible for the phenyl group to be in turn substituted by hydroxy, C_1-C_6alkylthio, C_1-C_6haloalkylthio, C_3-C_6alkenylthio, C_3-C_6haloalkenylthio, C_3-C_6alkynylthio, C_1-C_3alkoxy-C_1-C_3alkylthio, C_1-C_4alkylcarbonyl-C_1-C_3alkylthio, C_1-C_4alkoxycarbonyl-C_1-C_3alkylthio, cyano-C_1-C_3alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylsulfonyl, aminosulfonyl, C_1-C_2alkylaminosulfonyl, N,N-di(C_1-C_2alkyl)-aminosulfonyl, di(C_1-C_4alkyl)amino, halogen, cyano or by nitro, and the substituents on the nitrogen in the heterocyclic ring being other than halogen;
R_5 is hydroxy, C_1-C_6alkoxy, C_3-C_6cycloalkyloxy, C_1-C_6alkoxy-C_1-C_6alkoxy, C_1-C_6alkoxy-C_1-C_6alkoxy-C_1-C_6alkoxy or C_1-C_2alkylsulfonyloxy;
R_6, R_7, R_8, R_9, R_{10} R_{11}, R_{12}, R_{17}, R_{18} and R_{18b} are each independently of the others hydrogen, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbonyl, C_1-C_6-alkoxy-C_1-C_6alkyl, C_1-C_6alkoxy-C_1-C_6alkyl substituted by C_1-C_6alkoxy, benzyl, or phenyl, it being possible for phenyl and benzyl to be in turn substituted one or more times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, halogen, cyano, hydroxy or by

nitro; R_6 not being hydrogen when R_9 is hydrogen, C_1-C_6alkoxycarbonyl or C_1-C_6alkylcarbonyl;
or the group -R_1-X_1-R_2 together is C_1-C_6alkyl, C_2-C_6alkenyl, C_2-C_6haloalkenyl, C_2-C_6-alkynyl, C_2-C_6haloalkynyl, C_3-C_6cycloalkyl, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkylthio, C_1-C_6alkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkyl, C_1-C_6haloalkylthio, C_1-C_6haloalkyl-sulfinyl, C_1-C_6haloalkylsulfonyl, C_1-C_6alkoxycarbonyl, C_1-C_6alkylcarbonyl, C_1-C_6alkylamino, di(C_1-C_6alkyl)amino, C_1-C_6alkylaminosulfonyl, di(C_1-C_6alkyl)aminosulfonyl, -NH-S-R_{13}, -N-(C_1-C_4alkylthio)-R_{13}, -NH-SO-R_{14}, -N-(C_1-C_4alkylsulfonyl)-R_{14}, -NH-SO_2-R_{15}, -N-(C_1-C_4alkylsulfonyl)-R_{15}, nitro, cyano, halogen, hydroxy, amino, formyl, rhodano-C_1-C_6-alkyl, cyano-C_1-C_6alkyl, oxiranyl, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, C_1-C_6alkoxy-C_1-C_6-alkoxy, cyano-C_1-C_6alkenyloxy, C_1-C_6alkoxycarbonyloxy-C_1-C_6alkoxy, C_3-C_6alkynyloxy, cyano-C_1-C_6alkoxy, C_1-C_6alkoxycarbonyl-C_1-C_6alkoxy, C_1-C_6alkylthio-C_1-C_6alkoxy, alkoxycarbonyl-C_1-C_6alkylthio, alkoxycarbonyl-C_1-C_6alkylsulfinyl, alkoxycarbonyl-C_1-C_6-alkylsulfonyl, C_1-C_6alkylsulfonyloxy, C_1-C_6haloalkylsulfonyloxy, phenyl, benzyl, phenoxy, phenylthio, phenylsulfinyl, phenylsulfonyl, benzylthio, benzylsulfinyl or benzylsulfonyl, it being possible for the phenyl groups to be substituted one or more times by halogen, methyl, ethyl, trifluoromethyl, methoxy or by nitro;
or the group -R_1-X_1-R_2 together is a five- to ten-membered, monocyclic or fused bicyclic, ring system, which may be aromatic or partially saturated and which may contain from 1 to 4 hetero atoms selected from nitrogen, oxygen and sulfur, the ring system either being attached to the pyridine ring directly or being attached to the pyridine ring by way of a C_1-C_4alkylene chain, and it being possible for each ring system to contain no more than 2 oxygen atoms and no more than two sulfur atoms, and it being possible for the ring system itself to be substituted one, two or three times by C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_1-C_6alkoxy, C_1-C_6halo-alkoxy, C_3-C_6alkenyloxy, C_3-C_6alkynyloxy, mercapto, C_1-C_6alkylthio, C_1-C_6haloalkylthio, C_3-C_6alkenylthio, C_3-C_6haloalkenylthio, C_3-C_6alkynylthio, C_2-C_5alkoxyalkylthio, C_3-C_5acetylalkylthio, C_3-C_6alkoxycarbonylalkylthio, C_2-C_4cyanoalkylthio, C_1-C_6alkylsulfinyl, C_1-C_6haloalkylsulfinyl, C_1-C_6alkylsulfonyl, C_1-C_6haloalkylsulfonyl, aminosulfonyl, C_1-C_2alkylaminosulfonyl, C_2-C_4dialkylaminosulfonyl, C_1-C_3alkylene-R_{16}, N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, halogen, cyano, nitro, phenyl and by benzylthio, it being possible for phenyl and benzylthio to be in turn substituted on the phenyl ring by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy,

halogen, cyano or by nitro, and substituents on the nitrogen in the heterocyclic ring being other than halogen;

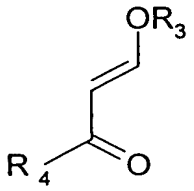
R_{13} is N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_3-C_6cycloalkyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;

R_{14} is N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_3-C_6cycloalkyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;

R_{15} is N(H)-C_1-C_6alkyl, N(H)-C_1-C_6alkoxy, N-(C_1-C_6alkyl)-C_1-C_6alkyl, N-(C_1-C_6alkyl)-C_1-C_6alkoxy, C_1-C_6alkoxy, C_1-C_6haloalkoxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_3-C_6alkenyl, C_3-C_6haloalkenyl, C_3-C_6alkynyl, C_3-C_6haloalkynyl, C_3-C_6cycloalkyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro;

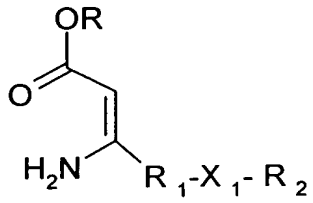
R_{16} is C_1-C_3alkoxy, C_2-C_4alkoxycarbonyl, C_1-C_3alkylthio, C_1-C_3alkylsulfinyl, C_1-C_3alkylsulfonyl or phenyl, it being possible for phenyl to be in turn substituted by C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy, C_1-C_3haloalkoxy, halogen, cyano or by nitro; and

R_{19} is hydrogen, hydroxy, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy, C_1-C_6alkylcarbonyl, C_1-C_6alkoxycarbonyl or C_1-C_6alkylsulfonyl; which process comprises reacting a compound of formula II



(II),

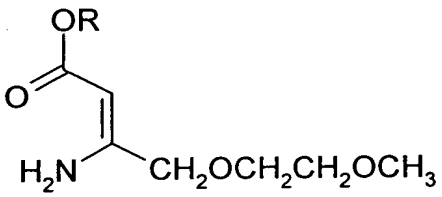
wherein R_3 is C_1-C_8alkyl or C_3-C_6cycloalkyl and R_4 is as defined for formula I, with a compound of formula III



(III),

wherein R, R_1, R_2 and X_1 are as defined for formula I, in an inert solvent in the presence of a proton source.

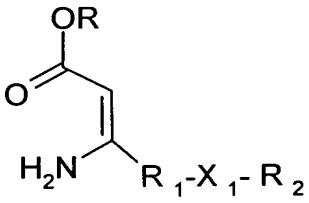
2. A compound of formula IIIa



(IIIa)

wherein R is as defined for formula III in claim 1.

3. Use of a compound of formula III

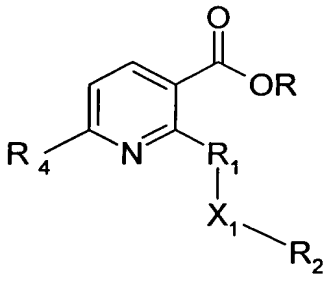


(III),

wherein R, R_1, R_2 and X_1 are as defined for formula I in claim 1, in the preparation of a compound of formula I according to claim 1.

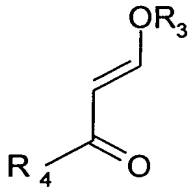
Abstract:

The present invention relates to a process for the preparation of compounds of formula I



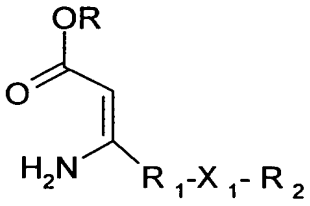
(I),

wherein the substituents are as defined in claim 1, by reaction of a compound of formula II



(II),

wherein R_3 is C_1-C_8alkyl or C_3-C_6cycloalkyl and R_4 is as defined for formula I, with a compound of formula III



(III),

wherein R, R_1, R_2 and X_1 are as defined for formula I in claim 1, in an inert solvent in the presence of a proton source.